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Baudry et al.

(10) **Patent No.: US 6,391,064 B1**
(45) **Date of Patent: May 21, 2002**

(54) **COMPOSITION FOR HAIR DYEING COMPRISING CONDENSATES OF QUINOLINE-5, 8-DIONES OR OF QUINOXALINE-5,8-DIONES AND SUBSTITUTED PYRROLES, ANILINES OR INDOLES**

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(73) Assignee: **L'Oreal S.A.**, Paris (FR)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

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(22) Filed: **Aug. 31, 1999**

(30) **Foreign Application Priority Data**

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(51) **Int. Cl.**[7] **A61K 7/13**; C07D 401/00; C07D 215/12; C07D 215/16

(52) **U.S. Cl.** **8/409**; 8/423; 8/424; 546/167; 546/168; 546/173; 546/177

(58) **Field of Search** 8/405, 406, 407, 8/423, 424, 429, 569, 574, 409, 567; 546/167, 168, 177, 173

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(57) **ABSTRACT**

The use of derivatives of quinoline- or quinoxaline-5,8-diones or -diols in cosmetics, especially for the dyeing of keratinous matter and, in particular, the hair. It also relates to novel compounds of this class. The invention is also directed to dyeing compositions comprising the said compounds and to the method of dyeing keratinous fibers.

17 Claims, No Drawings

COMPOSITION FOR HAIR DYEING COMPRISING CONDENSATES OF QUINOLINE-5, 8-DIONES OR OF QUINOXALINE-5,8-DIONES AND SUBSTITUTED PYRROLES, ANILINES OR INDOLES

The invention relates to the use of derivatives of quinoline- or quinoxaline-5,8-diones or -diols in cosmetics, especially for the dyeing of keratinous matter and, in particular, the hair. It also relates to novel compounds of this class. The invention is also directed to dyeing compositions comprising the said compounds and to the method of dyeing keratinous fibres.

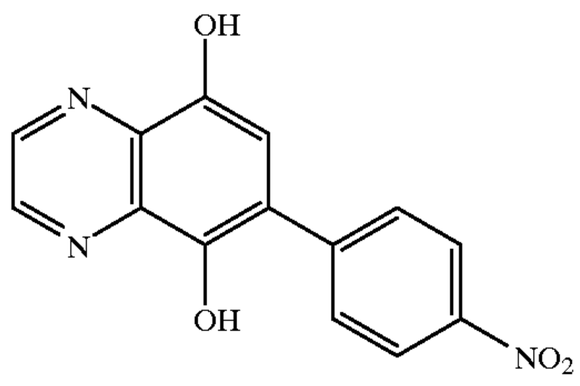
In the literature, adducts of pyrrole compounds and N,N-dialkylarylamines or N-alkylarylamines with quinoline-5,8-diones are known.

Thus J. Griffiths and C. Blackburn, in the journal *J. Chem. Res.* (*S*), 1982, pages 320–321, the disclosure of which is incorporated by reference herein, studied the reactions of 1,4-naphthoquinone and its derivatives with N,N-dialkylarylamines.

In the articles by K. Yoshida et al., *Bull. Chem. Soc. Jpn.*, 1988, 61, pages 4335–4340, and *Chem. Lett.*, 1987, pages 1191–1194, the disclosures of each which are incorporated by reference herein, it was shown that, in the absence of metal salts, the reaction of quinoline-5,8-dione with N,N-dialkylarylamines was slow and led to isomer mixtures of 6- and 7-[p-(dialkylamino)phenyl]quinoline-5,8-dione whereas, in the presence of metal salts, only the compounds arylated in position 6 were obtained. The reactions are generally conducted in acetic acid; in certain cases, a chloroform-ethanol/HCl mixture can also be used, according to the article by K. Yoshida et al. in *Chem. Lett.*, 1991, 2027–2030, the disclosure of which is incorporated by reference herein.

K. Yoshida et al. in *J. Chem. Soc. Perkin Trans. I*, 1992, 2713–2715, the disclosure of which is incorporated by reference herein, also studied the dioxo-5,8-quinolylpyrroles for their physiological properties and their colouring properties on an unspecified substrate. Furthermore, in the journal *J. Chem. Soc. Perkin Trans. I*, 1994, pages 2521–2523, the disclosure of which is incorporated by reference herein, K. Yoshida et al. took an interest in quinoline-5,8-diones carrying a substituent in position 6, for the purpose of a utility as a precursor of dyes which can be used in opto-electronics.

Furthermore, the only known derivative of quinoxaline corresponds to the following formula:



In accordance with the above text, adducts of pyrrole compounds and N,N-dialkylarylamines or N-alkylarylamines with quinoline-5,8-diones are already known, but no allusion whatsoever is made as regards their application in cosmetics.

On the other hand, the addition compounds of indoles with quinolinediones or quinoxalines are novel.

In the field of hair dyeing, dyes are sought which are reproducible, with rich and varied shades, thereby making it possible to obtain a wide pallet of colours capable of satisfying the formulator.

The inventors have now discovered that a new class of derivatives of quinoline- or quinoxaline-5,8-diones or -diols can be used for the dyeing of keratinous matter and, in particular, the hair. This new class, which is the subject of the invention, satisfies the above-described objectives and, moreover, is highly accessible, since the majority of these dyes are prepared in a single stage which is easy to implement.

The dyeings obtained with the aid of these dyes can exhibit reproducible, intensive and varied shades.

The present invention therefore provides for the use of compounds of general formulae (I) and (II) defined below in the dyeing of keratinous matter and, in particular, of the hair.

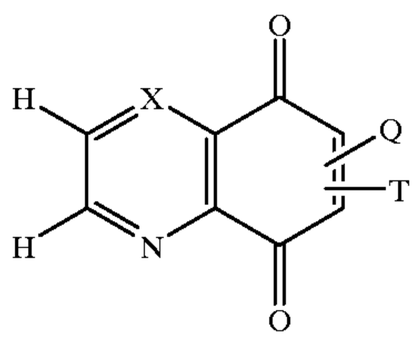
The present invention also provides novel compounds of this class.

The invention additionally provides dyeing compositions and a method of dyeing which employs them.

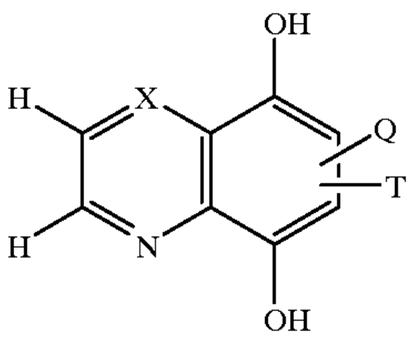
Other features, aspects and advantages of the invention will appear more clearly still on reading the description and various examples which follow.

One subject of the present invention is the use in the dyeing of keratinous matter and, in particular, of the hair of compounds of general formulae (I) and (II):

(I)

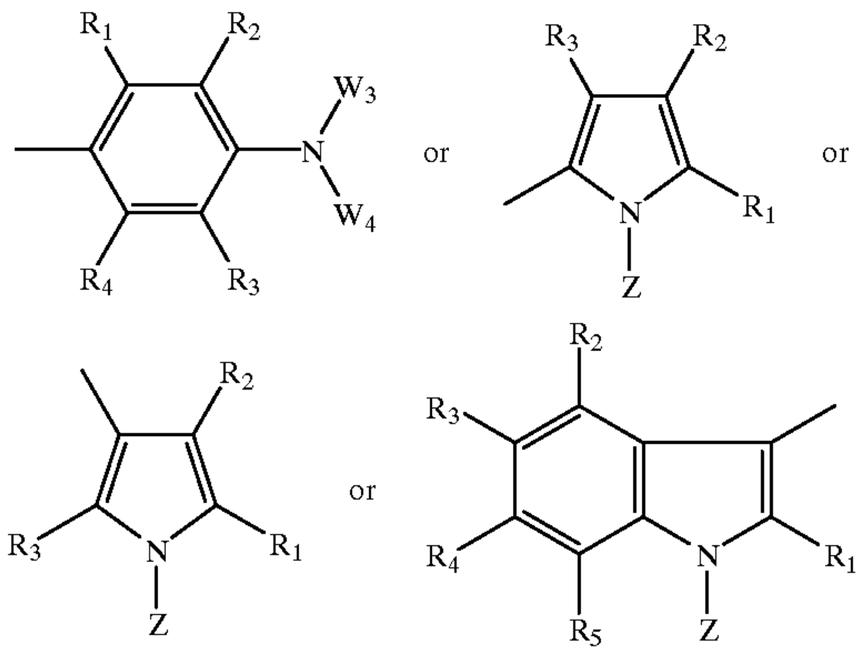


(II)



in which:

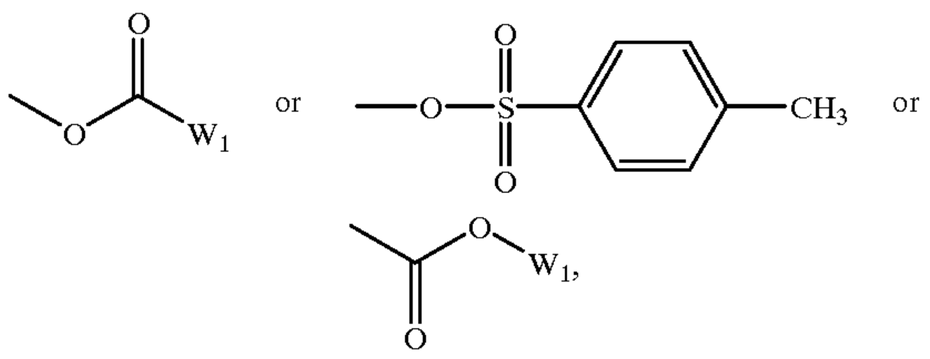
Q represents the groups



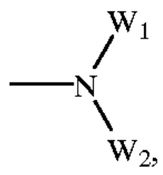
X represents the group CH or a nitrogen atom;

T represents a hydrogen atom, a halogen atom or a hydroxyl group;

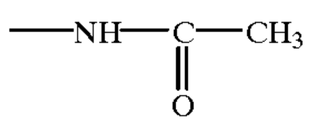
R_1, R_2, R_3, R_4 and R_5, which are identical or different, are selected from a hydrogen atom, C_1–C_4 alkoxy groups, amino groups —$N(W_1)(W_2)$, groups —NH—CO—W_1, groups —O—CO—W_1, a hydroxyl group, a carboxylic acid group, derivatives of a carboxylic acid group, such as esters, amides, mineral salts, and organic amine salts, halogen atoms, linear and branched C_1–C_4 alkyl groups optionally substituted by a substituent selected from nitrile groups, a carboxylic acid group, derivatives of a carboxylic acid group, such as esters, amides, mineral salts, and organic amine salts, a hydroxyl group, groups such as:



ether groups —$OSi(W_1)_3$, amino groups



and amido groups



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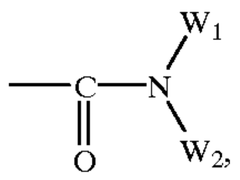
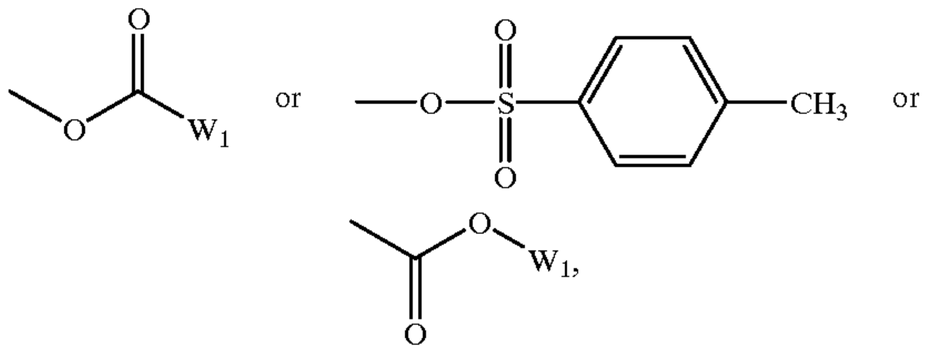
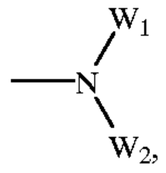


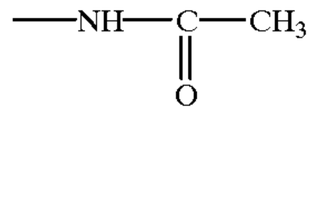
Z is selected from a hydrogen atom, a benzyl group, a phenyl group optionally substituted by a substituent selected from a hydroxyl group, groups —O—CO—W_1, amino groups —$N(W_1)(W_2)$, groups —NH—CO—W_1 and a nitrile group; linear and branched C_1–C_8 alkyl groups optionally substituted by a substituent selected from a nitrile group, a carboxylic acid group, derivatives of a carboxylic acid group, such as esters, amides, mineral salts, and organic amine salts, a hydroxyl group, groups such as:



ether groups —$OSi(W_1)_3$, amino groups



and amido groups



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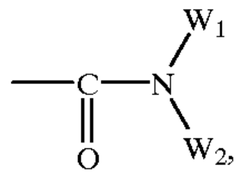


W_1 and W_2, which are identical or different, are selected from a hydrogen atom and linear and branched C_1–C_4 alkyl groups,

W_3 and W_4, which are identical or different, are selected from a hydrogen atom and linear and branched C_1–C_4 alkyl groups optionally substituted by at least one substituent selected from a hydroxyl group, groups —CO—O—W_1, groups —O—CO—W_1, and amino groups —$N(W_1)(W_2)$.

The C_1–C_4 alkyl groups or the C_1–C_4 alkyl moieties of alkoxy groups can be linear or branched and are selected in particular from the groups methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl and tert-butyl, preferably from the groups methyl, ethyl and n-butyl.

The C_1–C_8 alkyl groups can be linear or branched; they can be substituted by a nitrile group, a carboxylic acid group or its derivatives such as esters, amides, mineral salts and organic amine salts, a hydroxyl group, an ester group such as alkoxycarbonyl, carboxyl, alkylcarbonyloxy, formyloxy, tosyloxy, an amino group, an amido group such as aminocarbonyl or acetamido, or an ether group selected from trialkylsiloxy and siloxy groups.

These C_1–C_8 alkyl groups are selected in particular from the groups methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, pentyl, hexyl, heptyl and octyl, and preferably from the groups methyl and pentyl.

The halogen atoms are selected from chlorine, bromine, fluorine and iodine, and in particular chlorine.

Among the compounds of formulae (I) and (II) defined above, mention may be made in particular of the following compounds:

6-(1-pentyl-1H-pyrrol-2-yl)quinoline-5,8-dione,

6-(1-benzyl-1H-pyrrol-2-yl)quinoline-5,8-dione,

methyl 4-(5,8-dioxo-5,8-dihydroquinolin-6-yl)-2,5-dimethyl-1H-pyrrole-3-carboxylate,

N-[2-[2-(5,8-dioxo-5,8-dihydroquinolin-6-yl)pyrrol-1-yl]ethyl]acetamide,

6-(1-phenyl-1H-pyrrol-2-yl)quinoline-5,8-dione,

3-[2-(5,8-dioxo-5,8-dihydroquinolin-6-yl)pyrrol-1-yl]propionitrile,

6-chloro-7-(1-methyl-1H-pyrrol-2-yl)quinoline-5,8-dione,

6-(1,2-dimethyl-1H-indol-3-yl)quinoline-5,8-dione,

6-(1-benzyl-1H-indol-3-yl)quinoline-5,8-dione,

6-(2-phenyl-1H-indol-3-yl)quinoline-5,8-dione,

6-(2-methyl-1H-indol-3-yl)quinoline-5,8-dione,

6-(2-methyl-1H-indol-3-yl)quinoline-5,8-dione,

6-[p-(N,N-(2-diacetyloxyethyl)amino)phenyl]-quinoline-5,8-dione,

6-(1-methyl-1H-pyrrol-2-yl)quinoxaline-5,8-dione,

6-(1-methyl-1H-pyrrol-2-yl)quinoline-5,8-dione,

7-(1-methyl-1H-pyrrol-2-yl)quinoline-5,8-dione,

6-[p-(N,N-diethylamino)phenyl]quinoline-5,8-dione,

6-[p-(N,N-dimethylamino)phenyl]quinoline-5,8-dione

7-[p-(N,N-dimethylamino)phenyl]quinoline-5,8-dione

6-[4-(N,N-diethylamino)-3-isopropenylphenyl]-quinoline-5,8-dione,

6-[4-(N,N-diethylamino)-3-(N-acetylamino)phenyl] quinoline-5,8-dione,

6-[4-(N, N-dimethylamino)-3-isopropenylphenyl]-quinoline-5,8-dione,

6-[4-(N,N-di-n-butylamino)-3-hydroxyphenyl]-quinoline-5,8-dione,

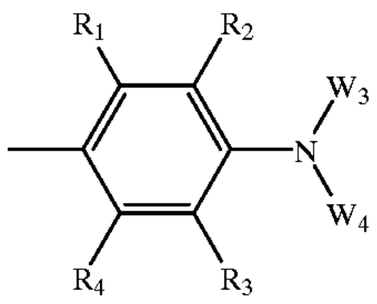
6-[p-(N-n-butylamino)phenyl]quinoline-5,8-dione,

6-[p-(N-methylamino)phenyl]quinoline-5,8-dione,

6-(1-methyl-1H-pyrrol-2-yl)quinoline-5,8-diol,

7-(1-methyl-1H-pyrrol-2-yl)quinoline-5,8-diol.

Among the compounds of formulae (I) and (II) which can be used in the present invention, more particular preference is given to the derivatives of formula (I) or (II) for which X represents CH; T represents H; Q is selected from:



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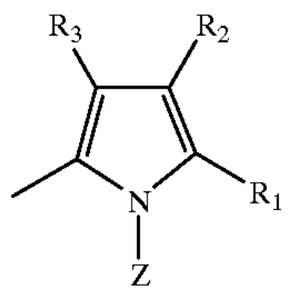

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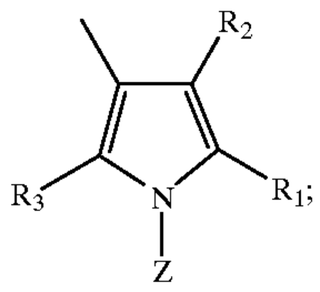
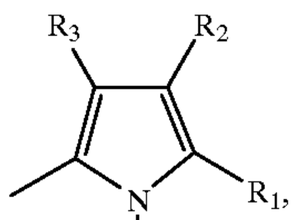


;

R_1 represents H or —OH; R_2, R_3, R_4 and R_5 each represent H; Z represents H or CH_3, phenyl, benzyl or 2-cyanoethyl; and W_3 and W_4 are selected from H and the groups methyl, ethyl and n-butyl.

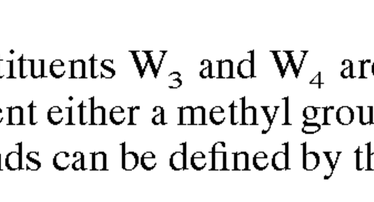
The novel compounds correspond to the formulae (I) and (II) of the invention, with the proviso that:

when Q represents



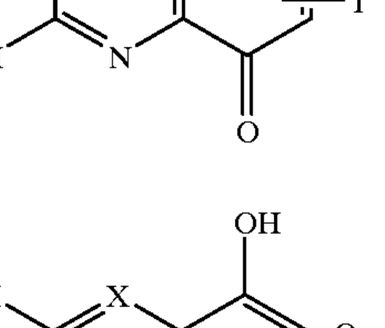
X=C and T=H, then Z is other than the methyl group;

when Q represents



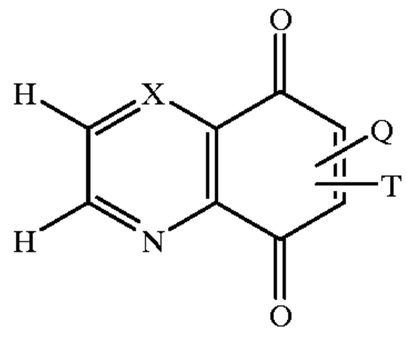
and one of the substituents W_3 and W_4 represents a hydrogen atom, the other substituent does not represent a methyl or n-butyl group; and

when Q represents

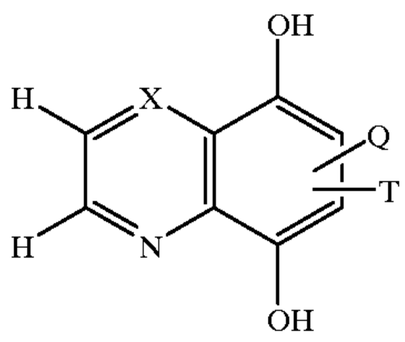


and the substituents W_3 and W_4 are identical, they do not represent either a methyl group or an ethyl group.

These compounds can be defined by the general formulae (III) and (IV):

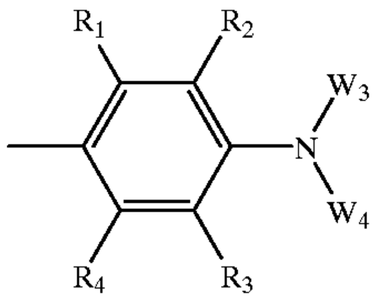


(III)



(IV)

in which Q represents



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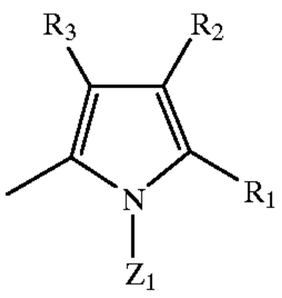

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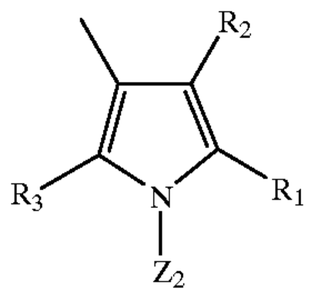

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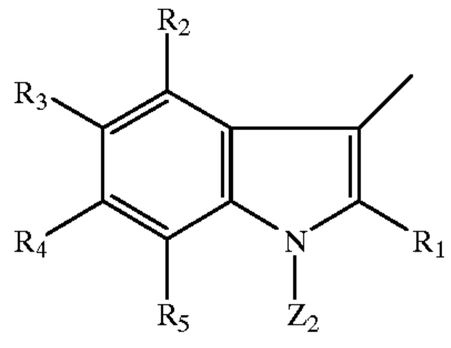
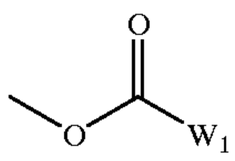


X represents the group CH or a nitrogen atom;

T represents a hydrogen atom, a halogen atom or a hydroxyl group;

R_1, R_2, R_3, R_4 and R_5, which are identical or different, are selected from a hydrogen atom, C_1–C_4 alkoxy groups, amino groups —$N(W_1)(W_2)$, groups —NH—CO—W_1, groups —O—CO—W_1, a hydroxyl group, a carboxylic acid group, derivatives of a carboxylic acid group, such as esters, amides, mineral salts, and organic amine salts, halogen atoms, linear and branched C_1–C_4 alkyl groups optionally substituted by a substituent selected from a nitrile group, a carboxylic acid group, derivatives of a carboxylic acid group, such as esters, amides, mineral salts and organic amine salts, a hydroxyl group, groups such as: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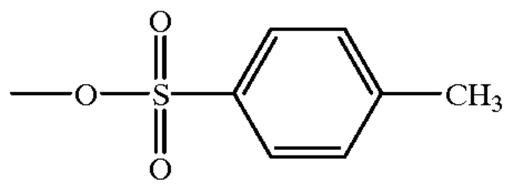
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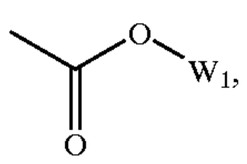
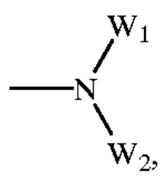
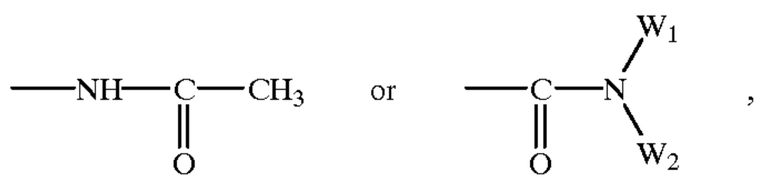


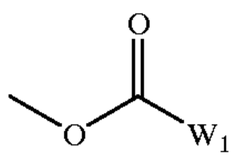
ether groups —$OSi(W_1)_3$, amino groups



amido groups



Z_2 represents a hydrogen atom, a benzyl group, a phenyl group optionally substituted by a substituent selected from a hydroxyl group, groups —CO—O—W_1, groups —O—CO—W_1, amino groups —$N(W_1)(W_2)$, amino groups —CO—$N(W_1)(W_2)$, amino groups —NH—CO—W_1 and a nitrile group; linear and branched C_1–C_8 alkyl groups optionally substituted by a substituent selected from a nitrile group, a carboxylic acid group, derivatives of a carboxylic acid group, such as esters, amides, mineral salts, and organic amine salts, a hydroxyl group, groups such as: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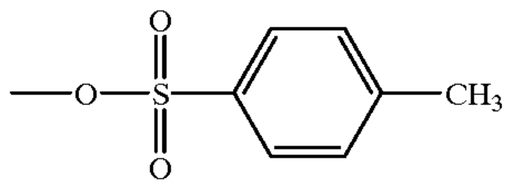
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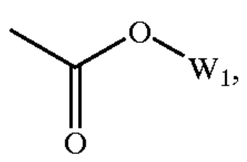
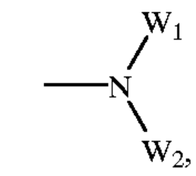
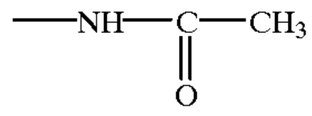


ether groups —$OSi(W_1)_3$, amino groups



amido groups



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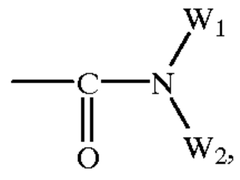


Z_1 has the same meanings as Z_2 with the proviso that Z_1 is not methyl in the cases where T=H and X=CH,

W_1 and W_2, which are identical or different, are selected from a hydrogen atom and linear and branched C_1–C_4 alkyl groups,

W_4 is selected from a hydrogen atom and linear and branched C_1–C_4 alkyl groups, optionally substituted by at least one substituent selected from a hydroxyl group, groups —CO—O—W_1, groups —O—CO—W_1, and amino groups —$N(W_1)(W_2)$, and

W_3 has the same meanings as W_4 with the proviso that, when one of the substituents W_3 and W_4 represents a hydrogen atom, the other substituent does not represent a methyl or n-butyl group; and, when the substituents W_3 and W_4 are identical, they do not represent either a methyl group or an ethyl group.

Among the novel compounds of formulae (III) and (IV) defined above, mention may be made in particular of the following compounds:

6-(1-pentyl-1H-pyrrol-2-yl)quinoline-5,8-dione,

6-(1-benzyl-1H-pyrrol-2-yl)quinoline-5,8-dione,

methyl 4-(5,8-dioxo-5,8-dihydroquinolin-6-yl)-2,5-dimethyl-1H-pyrrole-3-carboxylate,

N-[2-[2-(5,8-dioxo-5,8-dihydroquinolin-6-yl)pyrrol-1-yl] ethyl]acetamide,

6-(1-phenyl-1H-pyrrol-2-yl)quinoline-5,8-dione,

3-[2-(5,8-dioxo-5,8-dihydroquinolin-6-yl)pyrrol-1-yl] propionitrile,

6-chloro-7-(1-methyl-1H-pyrrol-2-yl)quinoline-5,8-dione,

6-(1,2-dimethyl-1H-indol-3-yl)quinoline-5,8-dione,

6-(1-benzyl-1H-indol-3-yl)quinoline-5,8-dione,

6-[p-(N,N-(2-diacetyloxyethyl)amino)phenyl]-quinoline-5,8-dione,

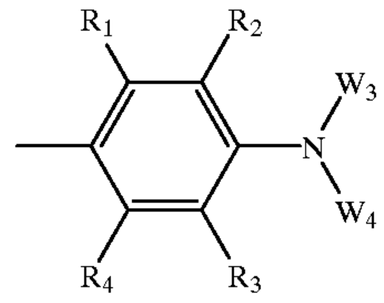
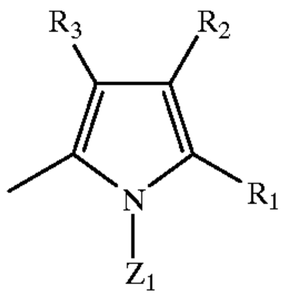
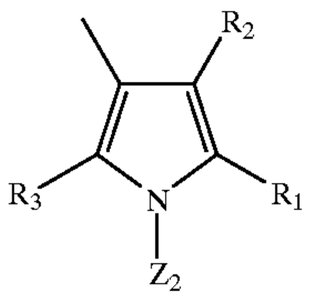
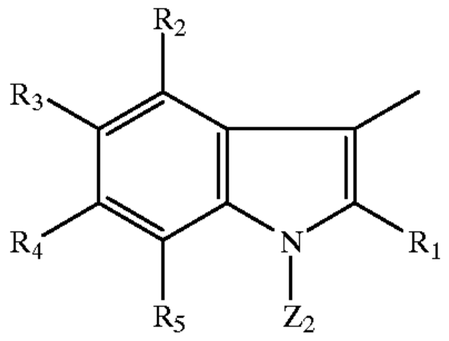
6-(2-phenyl-1H-indol-3-yl)quinoline-5,8-dione,

6-(1-methyl-1H-indol-3-yl)quinoline-5,8-dione,

6-(2-methyl-1H-indol-3-yl)quinoline-5,8-dione,

6-(1-methyl-1H-pyrrol-2-yl)quinoxaline-5,8-dione.

Among the compounds of formulae (III) and (IV) which can be used in the present invention, more particular preference is given to the derivatives of formula (III) or (IV) in which X represents CH or N; T represents H; Q is selected from:

R_1 is selected from H and the —CH_3 group; R_2 represents H or the group —COO—W_1, R_3 represents H or the methyl group, R_4 and R_5 each represent H; W_1 represents the —CH_3 group; Z_1 represents —C_5H_{11}, —$(CH_2)_2$—NH—$COCH_3$, —$(CH_2)_2$—CN or phenyl; Z_2 represents H or the —CH_3 and benzyl groups; and W_3 and W_4 can represent the group —$(CH_2)_2OCOW_1$.

The inventors have discovered that it is possible to dye keratinous fibres and, in particular, the hair by virtue of the compounds of formulae I and II. The colours obtained depend on the nature of the substituents Q and T that are used for carrying out the synthesis. By varying the nature of these substituents it is possible to produce a range of varied colours.

In accordance with the invention, the compounds of formula (I) or (II) are used for the direct dyeing, also known as semi-permanent colouring, of keratinous fibres and, in particular, the hair.

The compounds of formula (I) or (II) can be introduced as direct dyes into oxidation dyeing compositions to enrich with glints the dyeings obtained by means of the oxidation dye precursors and, optionally, of the couplers which are generally used in this type of dyeing.

The compounds of formula (II) are capable of being oxidized by atmospheric oxygen and are used for the dyeing of keratinous fibres, in particular the hair, in accordance with the method known as progressive dyeing, which comprises applying the compound of formula (II) to the fibres, in leaving it in the air generally for from 5 to approximately 45 minutes and, preferably, from 5 to approximately 30 minutes, on the said fibres, and in repeating this operation the desired number of times until, preferably, the desired coloration is obtained.

The invention also provides a dyeing composition, in particular a cosmetic dyeing composition, for keratinous matter and, in particular, for human keratinous fibres, which comprises, in a medium appropriate for dyeing, an effective amount of at least one of the compounds of formula (I) or (II) defined above.

For the purposes of the invention, the term keratinous matter refers principally to natural textile fibres such as wool and animal fur, the term human keratinous matter refers to the skin and nails, and the term human keratinous fibres refers to the hair, the eyebrows and the eyelashes. The invention is directed still more particularly to the hair of the head.

The compounds of formula (I) or (II) are generally present in proportions of between approximately 0.01 and 10%, inclusive, preferably between approximately 0.05 and 5%, inclusive, by weight, relative to the total weight of the dyeing composition.

The cosmetically acceptable medium is preferably a medium comprising water and/or organic solvents which are acceptable from the standpoint of cosmetology if the composition is intended for use in cosmetics, and, more particularly, alcohols (ethyl alcohol, isopropyl alcohol, benzyl alcohol), glycols or glycol ethers (propylene glycol or its ethers such as, for example, propylene glycol monomethyl ether, butylene glycol, dipropylene glycol and diethylene glycol alkyl ethers, such as, for example, diethylene glycol monoethyl ether or monobutyl ether, and ethylene glycol monomethyl, monoethyl and monobutyl ethers) in concentrations of generally between 0.5 and 25%, inclusive, preferably, between approximately 2 and 15%, inclusive, by weight relative to the total weight of the composition. The cosmetically acceptable medium may also include fats such as oils and waxes.

Fatty amides, such as mono- and diethanolamides and acids derived from copra, lauric acid or oleic acid, may also be added to the composition according to the invention, in concentrations of between approximately 0.05 and 10%, inclusive, by weight.

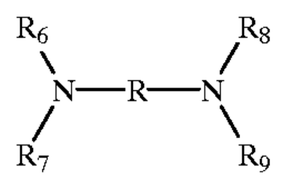
In order to obtain varied shades, the dyeing composition according to the invention may also include, in addition to the dyes of formula (I) or (II), one or more other direct dyes which are conventionally used, and in particular nitro-functional benzenic dyes, such as nitrophenylenediamines, nitrodiphenylamines, nitroanilines, nitro-functional phenol ethers or nitrophenols, nitropyridines, anthraquinone dyes, monoazo or disazo dyes, triarylmethane dyes, azine dyes, acridine dyes and xanthene dyes, or else metallic dyes. The proportion of all these other direct dyes of addition can vary between 0.05 and 10%, inclusive, by weight relative to the total weight of the dyeing composition.

The said dyeing composition may additionally comprise any other adjuvant which is used commonly in the dyeing of keratinous matter, and, for example, surfactants which are well known in the prior art and are of anionic, cationic, nonionic, amphoteric or zwitterionic type, or mixtures thereof, thickeners, antioxidants, perfumes, sequestrants, dispersants, conditioning agents, preservatives, opacifiers, etc.

The person skilled in the art will of course take care to select the above-mentioned complementary compound or compounds such that the advantageous properties intrinsic to the dyeing composition according to the invention are not, or not substantially, adversely affected by the intended addition or additions.

The dyeing composition according to the invention can be formulated at an acidic, neutral or alkaline pH, it being possible for the pH to vary, for example, from 2 to 11 and, preferably, from 2.5 to 10, and to be adjusted by means of basifying or acidifying agents which are well known in the prior art.

Among the basifying agents, mention may be made, by way of example, of aqueous ammonia, alkali metal carbonates, alkanolamines such as mono-, di- and triethanolamines and their derivatives, sodium hydroxide or potassium hydroxide, and the compounds of the following formula:



in which R represents a propylene group which is optionally substituted by a hydroxyl group or a C_1–C_4 alkyl group; and

R_6, R_7, R_8 and R_9, which are identical or different, are selected from a hydrogen atom, C_1–C_4 alkyl groups and C_1–C_4 hydroxyalkyl groups.

The acidifying agents which are used are conventionally known. Mention may be made, by way of example, of mineral acids or organic acids, such as hydrochloric acid, ortho-phosphoric acid, carboxylic acids such as tartaric acid, citric acid or lactic acid, and sulphonic acids.

When the composition is intended to be applied to human keratinous fibres, it can be presented in various forms, such as in the form of a liquid, cream or gel or any other form appropriate for carrying out the dyeing of keratinous fibres. In particular, it can be packaged under pressure in an aerosol can in the presence of a propellent, and can form a foam.

Another subject of the present invention relates to a method of dyeing human keratinous fibres and, more particularly, the hair by direct dyeing, which comprises leaving a dyeing composition comprising at least one compound of formula (I) or (II) to act on wet or dry keratinous fibres. The composition according to the invention can be used as a non-rinse composition; in other words, following application of the composition to the fibres, drying is carried out without rinsing beforehand. In the other modes of application, the composition is left to act on the fibres for a period generally varying between 3 and 60 minutes, inclusive, approximately, preferably between 5 and 45 minutes, inclusive, and the fibres are rinsed, optionally washed and rinsed again, and then dried.

An additional subject of the present invention relates to a method of progressive dyeing which comprises applying a dyeing composition comprising a compound of formula (II) defined above to the keratinous fibres, leaving the said composition in air for generally 5 to approximately 45 minutes and, preferably, from 5 to approximately 30 minutes, and then rinsing the fibres, optionally washing them, then rinsing them again, and then drying them.

By way of illustration and without any limitative character whatsoever, a number of examples will now be given of the preparation of compounds of formula (I) or (II) according to the invention, along with specific examples of dyeing compositions based on such compounds.

In order to prepare the compounds of formulae (I) to (IV), use is made generally of the procedure described by K. Yoshida, Y. Ueno, M. Suzuki, Y. Yoshida and Y. Kubo in *J. Chem. Soc. Perkin Trans. I*, 1992, 2713–2715, the disclosure of which is incorporated by reference herein, by reaction of quinoline-5,8-dione with a pyrrole derivative, selecting an appropriate molar ratio between the two reactants in solvent medium.

PREPARATION EXAMPLES

The compounds of the following examples were prepared with the aid of the general procedure described by K. Yoshida, Y. Ueno, M. Suzuki, Y. Yoshida and Y. Kubo in J. Chem. Soc. Perkin Trans. I, 1992, 2713–2715. This procedure was used for Examples 1 to 7.

A pyrrole derivative (25.12 mmol) and quinoline-5,8-dione in 50 ml of chloroform are added at room temperature to a solution of 3.14 mmol of ferric chloride in 60 ml of 20% aqueous acetic acid solution. The reaction medium is maintained with vigorous stirring and the progress of the reaction is monitored by thin-layer chromatography. At the end of the reaction, the organic phase is separated off, and the aqueous phase is extracted with 2×30 ml of chloroform. The combined organic phases are washed with aqueous sodium carbonate solution and then with water before being dried over magnesium sulphate, filtered and concentrated under reduced pressure. The crude product thus obtained is purified by chromatography on a silica gel column.

Example 1

Preparation of 6-(1-Methyl-1H-pyrrol-2-yl) quinoline-5,8-dione

The compound of Example 1 is prepared following the procedure described above. After 5 minutes of reaction, 6-(1-methyl-1H-pyrrol-2-yl)quinoline-5,8-dione is isolated. The yield is 62%.

The structure of the compound was verified by ^1H and ^{13}C NMR spectroscopy.

^1H NMR, 200 MHz ($CDCl_3$, δ ppm): 3.73 (s, 3H), 6.30 (d.d, 1H), 6.77 (d.d, 1H), 6.94 (m, 1H), 7.03 (s, 1H), 7.70 (d.d, 1H), 8.49 (d, 1H), 9.05 (d, 1H). ^{13}C NMR, 50 MHz ($CDCl_3$, δ ppm): 36.4; 109.9; 118.5; 125.9; 127.4; 129.5; 130.2; 131.0; 135.1; 136.4; 138.6; 154.6; 183.0; 183.9. Melting point: 167–168° C.

Example 2

Preparation of 6-(1-Pentyl-1H-pyrrol-2-yl) quinoline-5,8-dione

After 5 minutes of reaction, 6-(1-pentyl-1H-pyrrol-2-yl) quinoline-5,8-dione is isolated, in accordance with the above procedure, in the form of an oil. The yield is 18%.

^1H NMR, 200 MHz ($CDCl_3$, δ ppm): 0.83 (t, 3H), 1.22 (m, 4H), 1.73 (q, 2H), 3.96 (t, 2H), 6.30 (d.d, 1H), 6.67 (d.d, 1H), 7.00 (m, 2H), 7.70 (d.d, 1H), 8.49 (d.d, 1H), 9.05 (d.d, 1H).

Example 3

Preparation of 6-(1-Benzyl-1H-pyrrol-2-yl) quinoline-5,8-dione

After 5 minutes of reaction, 6-(1-benzyl-1H-pyrrol-2-yl) quinoline-5,8-dione is isolated in accordance with the above procedure. The yield is 53%.

^1H NMR, 200 MHz ($CDCl_3$, δ ppm): 5.21 (s, 2H), 6.36 (d.d, 1H), 6.73 (d.d, 1H), 6.92 (s, 1H), 6.93–7.01 (m, 3H), 7.18–7.24 (m, 3H), 7.68 (d.d, 1H), 8.47 (d.d, 1H), ^{13}C NMR, 50 MHz ($CDCl_3$, δ ppm): 52.3; 110.0; 118.0; 126.0; 126.7; 127.4; 127.9; 128.8; 129.3; 131.9; 135.0; 137.1; 139.4; 147.4; 154.5; 183.0; 183.9. Melting point: 172–173° C.

Example 4

Preparation of Methyl 4-(5,8-Dioxo-5,8-dihydroquinolin-6-yl)-2,5-dimethyl-1H-pyrrole-3-carboxylate

After 5 hours of reaction, methyl 4-(5,8-dioxo-5,8-dihydroquinolin-6-yl)-2,5-dimethyl-1H-pyrrole-3-carboxylate is isolated in accordance with the above procedure. The yield is 58%.

^1H NMR, 200 MHz ($CDCl_3$, δ ppm): 2.25 (s, 3H), 2.52 (s, 3H), 3.63 (s, 3H), 6.94 (s, 1H), 7.70 (d.d, 1H), 8.36 (m, 1H), 8.48 (d.d, 1H), 9.05 (d.d, 1H). Melting point: 237–241° C.

Example 5

Preparation of N-[2-[2-(5,8-Dioxo-5,8-dihydroquinolin-6-yl)pyrrol-1-yl]ethyl]acetamide

After 20 minutes of reaction, N-[2-[2-(5,8-dioxo-5,8-dihydroquinolin-6-yl)pyrrol-1-yl]ethyl]-acetamide is isolated in accordance with the above procedure. The yield is 41%.

^{1}H NMR, 200 MHz ($CDCl_3$, δ ppm): 1.89 (s, 3H), 3.51 (m, 2H), 4.13 (t, 2H), 5.90 (s large, 1H), 6.33 (d.d, 1H), 6.61 (d.d, 1H), 7.00–7.03 (m, 2H), 7.71 (d.d, 1H), 8.48 (d.d, 1H), 9.04 (d.d, 1H). Melting point: 164–165° C.

Example 6

Preparation of 6-(1-Phenyl-1H-pyrrol-2-yl) quinoline-5,8-dione

After 6 hours of reaction, 6-(1-phenyl-1H-pyrrol-2-yl) quinoline-5,8-dione is isolated in accordance with the above procedure. The yield is 64%.

^{1}H NMR, 200 MHz ($CDCl_3$, δ ppm): 6.44–6.48 (m, 2H), 6.93 (d.d, 1H), 7.31–7.47 (m, 6H), 7.81 (d.d, 1H), 8.27 (d.d, 1H), 8.99 (d.d, 1H). ^{13}C NMR, 50 MHz ($CDCl_3$, δ ppm): 111.1; 120.4; 125.0; 125.1; 127.4; 127.8; 129.5; 129.8; 130.2; 131.7; 135.0; 138.3; 139.9; 147.4; 154.5; 182.7; 183.8. Melting point: 132–134° C.

Example 7

Preparation of 3-[2-(5,8-Dioxo-5,8-dihydroquinolin-6-yl)pyrrol-1-yl]propionitrile.

After 30 minutes of reaction, 3-[2-(5,8-dioxo-5,8-dihydroquinolin-6-yl)pyrrol-1-yl]propionitrile is isolated in accordance with the above procedure. The yield is 44%.

^{1}H NMR, 200 MHz ($CDCl_3$, δ ppm): 2.88 (t, 2H), 4.22 (t, 2H), 6.37 (d.d, 1H), 6.59 (d.d, 1H), 7.08–7.11 (m, 2H), 7.73 (d.d, 1H), 8.50 (d.d, 1H), 9.08 (d.d, 1H). ^{13}C NMR, 50 MHz ($CDCl_3$, δ ppm): 20.2; 44.0; 111.2; 117.0; 117.4; 126.1; 127.6; 127.7; 129.2; 134.2; 135.2; 139.4; 147.5; 154.9; 182.9; 184.1. Melting point: 166–167° C.

Example 8

Preparation of 6-(1-Methyl-1H-pyrrol-2-yl) quinoline-5,8-diol

6-(1-Methyl-1H-pyrrol-2-yl)quinoline-5,8-diol was prepared in accordance with the procedure described by K. Yoshida et al. in the article in *J. Chem. Perkin Trans. I*, 1994, 2521–2523.

Melting point: 142–143° C.

Example 9

Preparation of 6-Chloro-7-(1-methyl-1H-pyrrol-2-yl)quinoline-5,8-dione

A solution of 2.58 mmol of 6-chloroquinoline-5,8-dione with 20.7 mmol of 1-methylpyrrole in 50 ml of acetic acid is stirred at room temperature for 24 hours. The medium is subsequently concentrated under reduced pressure, the residue is extracted with chloroform and the combined organic phases are washed in succession with aqueous sodium carbonate solution and then water before being dried over magnesium sulphate, filtered and concentrated under vacuum. The crude product obtained is purified by chromatography on a silica gel column to give 6-chloro-7-(1-methyl-1H-pyrrol-2-yl)quinoline-5,8-dione with a yield of 40%.

^{1}H NMR, 200 MHz ($CDCl_3$, δ ppm): 3.57 (s, 3H), 6.34 (d.d, 1H), 6.61 (d.d, 1H), 6.94 (t, 1H), 7.75 (d.d, 1H), 8.56 (d.d, 1H), 9.10 (d.d, 1H). Melting point: 168–169° C.

Examples 10 to 14 describe the condensation of indoles onto the quinoline-5,8-dione ring system. The monocondensation was verified by mass spectrometry.

Example 10

Preparation of 6-(1,2-Dimethyl-1H-indol-3-yl) quinoline-5,8-dione

The product is prepared in accordance with the general procedure of Examples 1 to 7 with a yield of 46%.

Melting point: 213–214° C.

Example 11

Preparation of 6-(1-Benzyl-1H-indol-3-yl)quinoline-5,8-dione

The product is prepared in accordance with the general procedure with a yield of 51%.

Melting point: 179–180° C.

Example 12

Preparation of 6-(2-Phenyl-1H-indol-3-yl)quinoline-5,8-dione

The product is prepared in accordance with the general procedure with a yield of 62%.

Melting point: 330° C. (decomposition).

Example 13

Preparation of 6-(1-Methyl-1H-indol-3-yl)quinoline-5,8-dione

The product is prepared in accordance with the general procedure with a yield of 54%.

Melting point: 215–217° C.

Example 14

Preparation of 6-(2-Methyl-1H-indol-3-yl)quinoline-5,8-dione

The product is prepared in accordance with the general procedure with a yield of 58%.

Melting point: 221–223° C.

The procedure used for the preparation of the 6-[p-(dialkylamino)phenyl]quinoline-5,8-diones of Examples 15 and 16 is that described by K. Yoshida et al. in the article in *Bull. Chem. Soc. Jap*. 1988, 61, 4335.

Example 15

Preparation of 6-[p-(Diethylamino)phenyl] quinoline-5,8-dione

The product is prepared in accordance with the above procedure with a yield of 78%.

^{1}H NMR, 200 MHz (DMSO d_6, δ ppm): 1.20 (t, 6H), 3.44 (q, 4H), 6.72 (d, 2H), 7.18 (s, 1H), 7.62 (d, 2H), 7.62 (d.d, 1H), 8.50 (d.d, 1H), 9.04 (d.d, 1H). Melting point: 136–137° C.

Example 16

Preparation of 6-[p-(N,N-(2-diacetyloxyethyl) amino)phenyl]quinoline-5,8-dione

The product is prepared in accordance with the above procedure with a yield of 64%. It is isolated in the form of a viscous, dark violet oil.

^{1}H NMR, 200 MHz (DMSO d_6, δ ppm): 2.53 (s, 6H), 3.62–3.68 (m, 4H), 4.24–4.27 (m, 4H), 6.76–6.88 (m, 2H), 7.11–7.26 (m, 2H), 7.59–7.72 (m, 2H), 8.49–8.53 (m, 1H), 9.06 (m, 1H).

Example 17

Preparation of 6-(1-Methyl-1H-pyrrol-2-yl) quinoxaline-5,8-dione

0.81 g of N-methylpyrrole and 200 mg of quinoxaline-5, 8-dione in solution in 50 ml of chloroform are added rapidly to a solution of 338 mg of $FeCl_3 \times 6H_2O$ in a water (48 ml)/acetic acid (12 ml) mixture. The medium is stirred vigorously for 10 minutes and then the organic phase is separated off.

The aqueous phase is extracted twice with chloroform, and the combined organic phases are washed with aqueous sodium carbonate solution and then water before being dried over magnesium sulphate, filtered and concentrated under vacuum. The residue thus obtained is purified by chromatography on a silica gel column to give 6-(1-methyl-1H-pyrrol-2-yl)quinoxaline-5,8-dione with a yield of 68%.

^1H NMR, 200 MHz ($CDCl_3$, δ ppm): 3.77 (s, 3H), 6.34 (d.d, 1H), 6.88 (d.d, 1H), 6.99 (m, 1H), 7.13 (s, 1H), 9.05 (s, 2H). Melting point: 161–162° C.

EXAMPLES OF DYEING COMPOSITIONS

Examples of Dyeing at an Acidic pH

The general formulation at acid pH is as follows:

	Amount
Compound from Preparation Example (see Table 1)	2.24×10^{-3} mol
Benzyl alcohol	10 g
Ethyl alcohol	21 g
Glycerol	5 g
Hydroxyethylcellulose sold by the company Union Carbide under the name CELLOSIZE QP 4400 H	2.3 g
Citric acid	1.4 g
Water q.s. to	100 g

The dyeing procedure comprises applying the preparation, whose pH is approximately 3, at room temperature to natural grey hair, permed or otherwise, or to bleached hair, in a proportion of 3 grams per gram of hair. After having left the composition to act for 30 minutes, the locks were rinsed and then dried. The dyeing results are collated in Table 1.

TABLE 1

Test compound	Mass in g %	Natural grey hair	Bleached hair	Permed grey hair
Compound of Ex. 3	0.704		rosewood	
Compound of Ex. 15	0.686	blue	blue	blue
Compound of Ex. 4	0.695		rosewood	
Compound of Ex. 5	0.693		strawberry	
Compound of Ex. 6	0.673	rosewood	orange-red	rosewood
Compound of Ex. 7	0.621		pale pink	
Compound of Ex. 9	0.611		pinky beige	
Compound of Ex. 1	0.534	rosewood	dark-purplish red	rosewood

Examples of Dyeing at a pH of 7.5

The general formulation at pH 7.5 is as follows:

	Amount
Compound from Preparation Example (see Table 2)	2.24×10^{-3} mol
Benzyl alcohol	10 g
Ethyl alcohol	21 g
Glycerol	5 g
Hydroxyethylcellulose sold by the company Union Carbide under the name CELLOSIZE QP 4400 H	2.3 g
K_2HPO_4/KH_2HPO_4 (1.5M/1M) buffer	10 g
Water q.s. to	100 g

The dyeing procedure comprises applying the preparation, whose pH is approximately 7.5, at room temperature to natural grey hair, permed or otherwise, or to bleached hair, in a proportion of 3 grams per gram of hair. After having left the composition to act for 30 minutes, the locks were rinsed and then dried. The dyeing results are collated in Table 2.

TABLE 2

Test compound	Mass in g %	Natural grey hair	Bleached hair	Permed grey hair
Compound of Ex. 15	0.686	green-blue	blue	blue
Compound of Ex. 1	0.534	rosewood	dark-purplish red	rosewood

Examples of Dyeing at Basic pH

The general formulation at pH 8.6 is as follows:

	Amount
Compound from Preparation Example (see Table 3)	2.24×10^{-3} mol
Benzyl alcohol	10 g
Ethyl alcohol	21 g
Glycerol	5 g
Hydroxyethylcellulose sold by the company Union Carbide under the name CELLOSIZE QP 4400 H	2.3 g
Aminopropanediol/HCl (1M/0.035M) buffer	10 g
Water q.s. to	100 g

The dyeing procedure comprises applying the preparation, whose pH is approximately 8.6, at room temperature to natural grey hair, permed or otherwise, or to bleached hair, in a proportion of 3 grams per gram of hair. After having left the composition to act for 30 minutes, the locks were rinsed and then dried. The dyeing results are collated in Table 3.

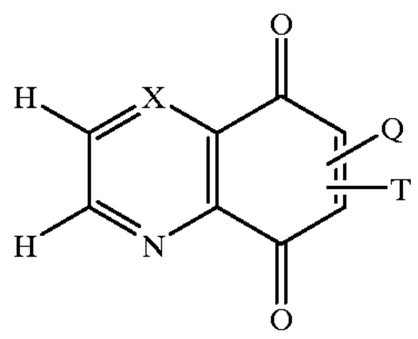
TABLE 3

Test compound	Mass in g %	Natural grey hair	Bleached hair	Permed grey hair
Compound of Ex. 15	0.686	green-blue	blue	blue
Compound of Ex. 1	0.534	rosewood	dark-purplish red	rosewood

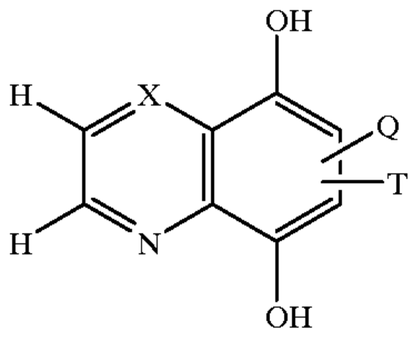
What is claimed is:

1. A composition for the dyeing of keratin fibers comprising a cosmetically acceptable medium and an amount effective for dyeing keratin fibers of at least one dye chosen from general formulae (I) and (II) below:

(I)



(II)

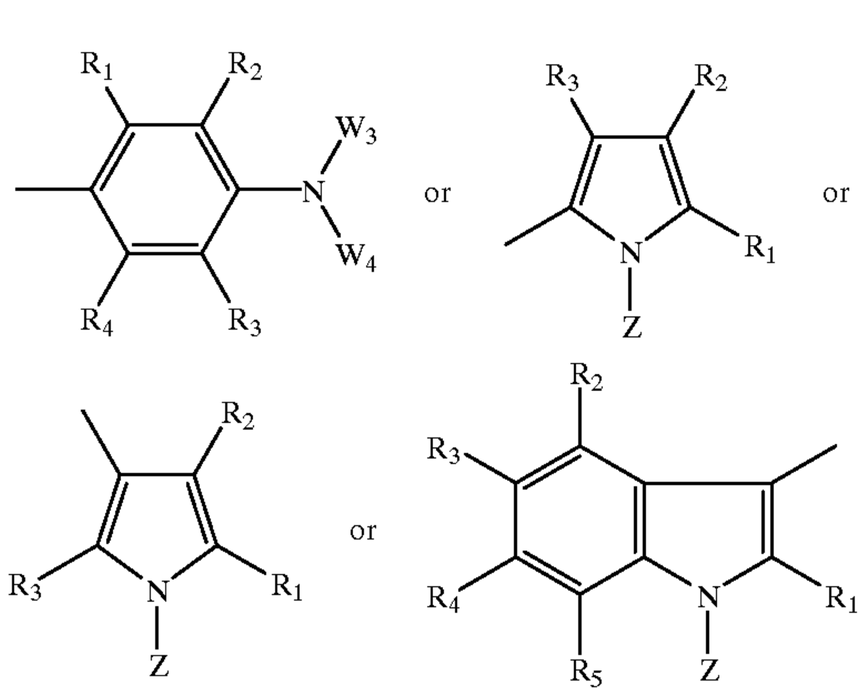


wherein:

T is chosen from a hydrogen atom, halogen atoms and a hydroxyl group;

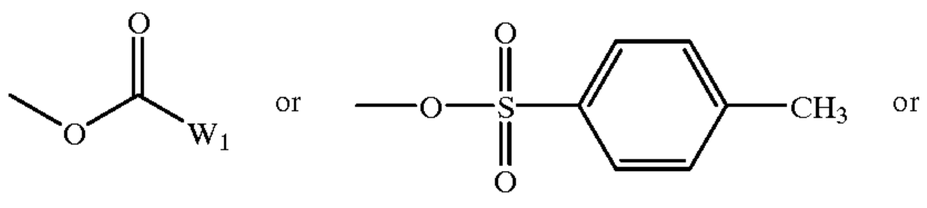
X is chosen from a —CH group and a nitrogen atom;

Q is chosen from the groups below:



wherein in said groups:

R_1, R_2, R_3, R_4 and R_5, which are identical or different, are selected from a hydrogen atom, C_1–C_4 alkoxy groups, amino groups —$N(W_1)(W_2)$, groups —NH—CO—W_1, groups —O—CO—W_1, a hydroxyl group, a carboxylic acid group, derivatives of a carboxylic acid group, halogen atoms, linear and branched C_1–C_4 alkyl groups optionally substituted by a substituent selected from nitrile groups, a carboxylic acid group, derivatives of a carboxylic acid group, a hydroxyl group, groups:



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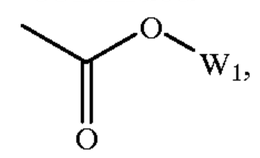
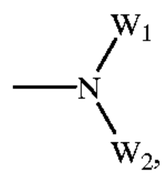
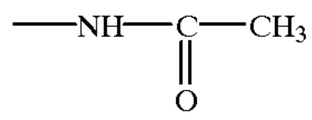
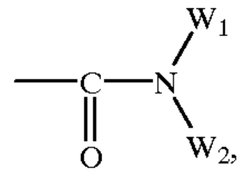


ether groups —$OSi(W_1)_3$, amino groups

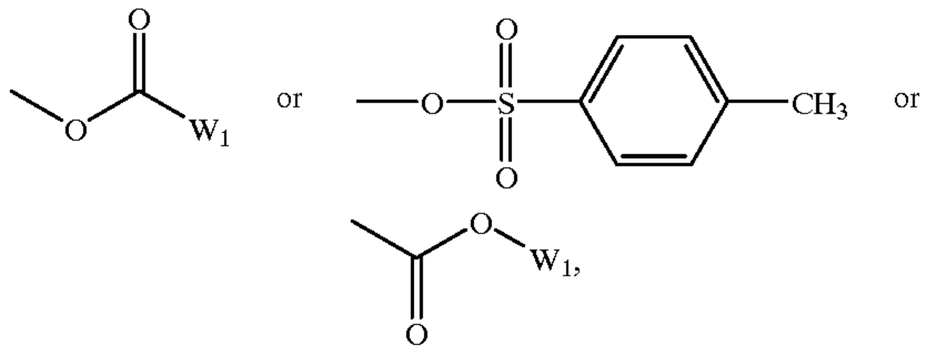


and amido groups



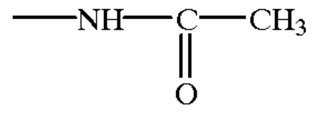


Z is selected from a hydrogen atom, a benzyl group, a phenyl group optionally substituted by a substituent selected from a hydroxyl group, groups —O—CO—W_1, amino groups —$N(W_1)(W_2)$, groups —NH—CO—W_1 and a nitrile group; linear and branched C_1–C_8 alkyl groups optionally substituted by a substituent selected from a nitrile group, a carboxylic acid group, derivatives of a carboxylic acid group, a hydroxyl group, groups:

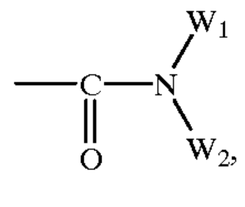


ether groups —$OSi(W_1)_3$, amino groups

and amido groups



or



W_1 and W_2, which are identical or different, are selected from a hydrogen atom and linear and branched C_1–C_4 alkyl groups,

W_3 and W_4, which are identical or different, are selected from a hydrogen atom and linear and branched C_1–C_4 alkyl groups optionally substituted by at least one substituent selected from a hydroxyl group, groups —CO—O—W_1, groups —O—CO—W_1, and amino groups —N(W_1)(W_2).

2. The composition according to claim **1**, wherein said keratin fibers are human keratin fibers.

3. The composition according to claim **2**, wherein said human keratin fibers are human hair.

4. The composition according to claim **1**, wherein said derivatives of a carboxylic acid group are chosen from esters, amides, mineral salts and organic amine salts.

5. The composition according to claim **1**, wherein said at least one dye chosen from formulae (I) and (II) is chosen from:

6-(1-pentyl-1H-pyrrol-2-yl)quinoline-5,8-dione,

6-(1-benzyl-1H-pyrrol-2-yl)quinoline-5,8-dione,

methyl 4-(5,8-dioxo-5,8-dihydroquinolin-6-yl)-2,5-dimethyl-1H-pyrrole-3-carboxylate,

N-[2-[2-(5,8-dioxo-5,8-dihydroquinolin-6-yl)pyrrol-1-yl]ethyl]acetamide,

6-(1-phenyl-1H-pyrrol-2-yl)quinoline-5,8-dione,

3-[2-(5,8-dioxo-5,8-dihydroquinolin-6-yl)pyrrol-1-yl]propionitrile,

6-chloro-7-(1-methyl-1H-pyrrol-2-yl)quinoline-5,8-dione,

6-(1,2-dimethyl-1H-indol-3-yl)quinoline-5,8-dione,

6-(1-benzyl-1H-indol-3-yl)quinoline-5,8-dione,

6-(2-phenyl-1H-indol-3-yl)quinoline-5,8-dione,

6-(1-methyl-1H-indol-3-yl)quinoline-5,8-dione,

6-(2-methyl-1H-indol-3-yl)quinoline-5,8-dione,

6-[p-(N,N-(2-diacetyloxyethyl)amino)phenyl]-quinotine-5,8-dione,

6-(1-methyl-1H-pyrrol-2-yl)quinoxaline-5,8-dione,

6-(1-methyl-1H-pyrrol-2-yl)quinoline-5,8-dione,

7-(1-methyl-1H-pyrrol-2-yl)quinoline-5,8-dione,

6-[p-(N,N-diethylamino)phenyl]quinoline-5,8-dione,

6-[p-(N,N-dimethylamino)phenyl]quinoline-5,8-dione,

7-[p-(N,N-dimethylamino)phenyl]quinoline-5,8-dione,

6-[4-(N,N-diethylamino)-2-isopropenylphenyl]-quinoline-5,8-dione,

6-[4-(N,N-diethylamino)-2-(N-acetylamino)phenyl]quinoline-5,8-dione,

6-[4-(N,N-dimethylamino)-2-isopropenylphenyl]-quinoline-5,8-dione,

6-[4-(N,N-di-n-butylamino)-2-hydroxyphenyl]-quinoline-5,8-dione,

6-[p-(N-n-butylamino)phenyl]quinoline-5,8-dione,

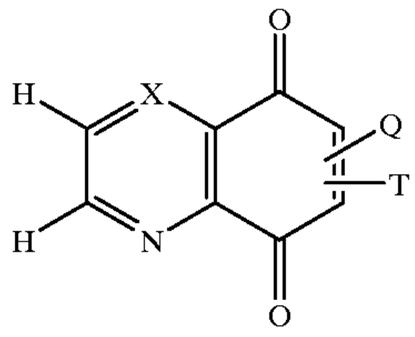
6-[p-(N-methylamino)phenyl]quinoline-5,8-dione,

6-(1-methyl-1H-pyrrol-2-yl)quinoline-5,8-diol, and

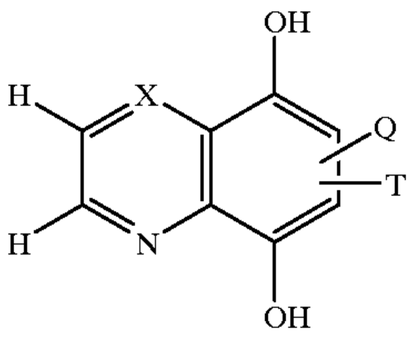
7-(1-methyl-1H-pyrrol-2-yl)quinoline-5,8-diol.

6. The composition according to claim **1**, wherein said at least one dye of formulae (I) and (II) is chosen from:

(I)



(II)

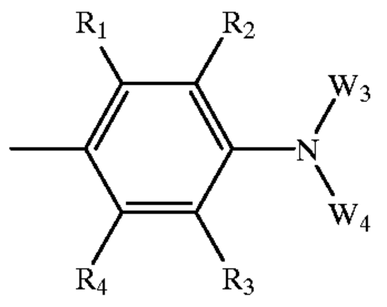


wherein,

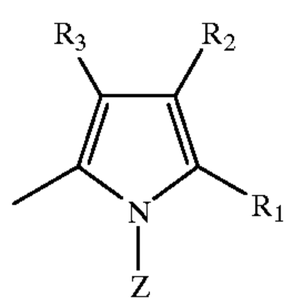
X is a —CH group;

T is a hydrogen atom;

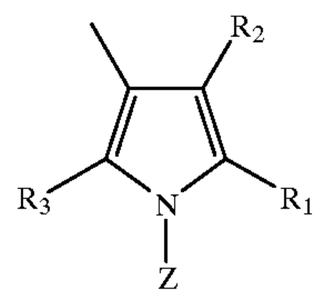
Q is chosen from the formulae below:



or



or



wherein,

R_1 is chosen from a hydrogen atom and —OH;

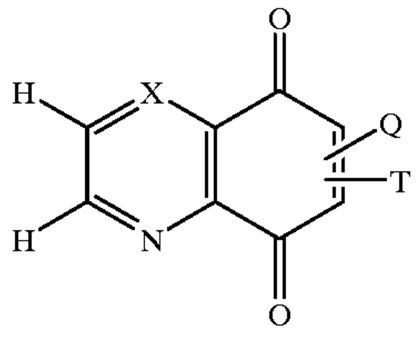
R_2, R_3, R_4, and R_5 are hydrogen atoms;

Z is chosen from a hydrogen atom and —CH_3, phenyl, benzyl and 2-cyanoethyl groups; and

W_3 and W_4 are chosen from a hydrogen atom and methyl, ethyl and n-butyl groups.

7. A composition for the dyeing of keratin fibers comprising a cosmetically acceptable medium and an amount effective for dyeing keratin fibers of at least one dye chosen from general formulae (III) and (IV) below:

(III)



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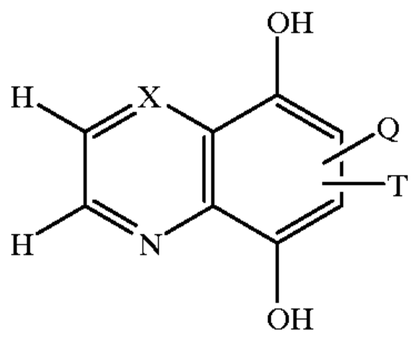


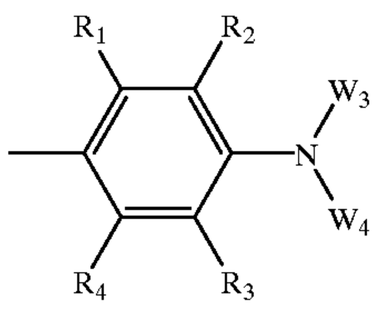
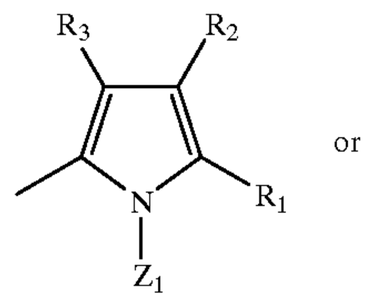
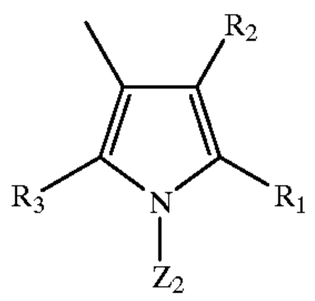
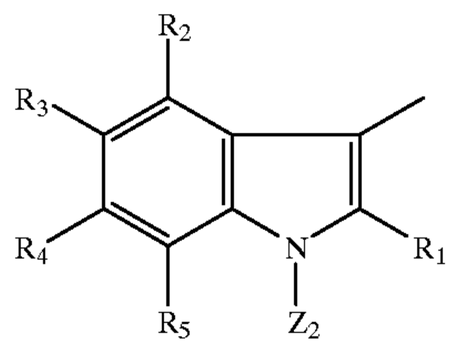
(IV)

wherein,

X represents the group CH or a nitrogen atom;

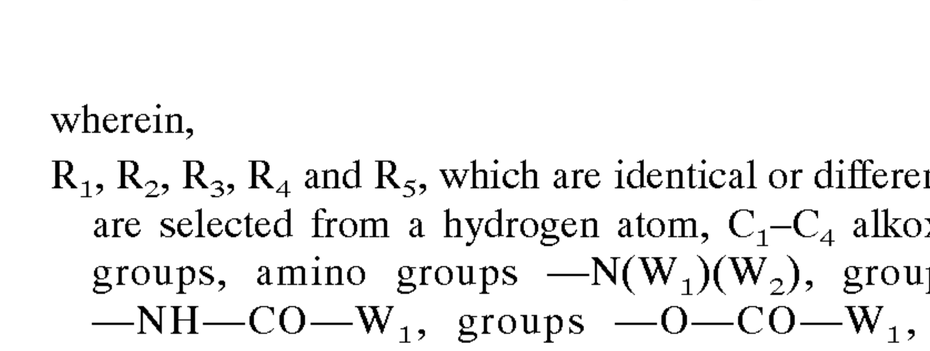
T represents a hydrogen atom, a halogen atom or a hydroxyl group;

Q is chosen from the formulae below:

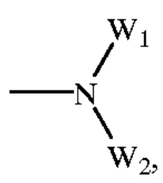





wherein,

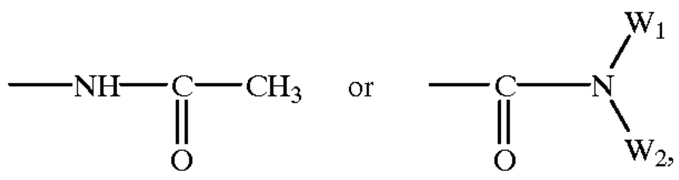
R_1, R_2, R_3, R_4 and R_5, which are identical or different, are selected from a hydrogen atom, C_1–C_4 alkoxy groups, amino groups —$N(W_1)(W_2)$, groups —NH—CO—W_1, groups —O—CO—W_1, a hydroxyl group, a carboxylic acid group, derivatives of a carboxylic acid group, halogen atoms, linear and branched C_1–C_4 alkyl groups optionally substituted by a substituent selected from a nitrile group, a carboxylic acid group, derivatives of a carboxylic acid group, a hydroxyl group, groups:



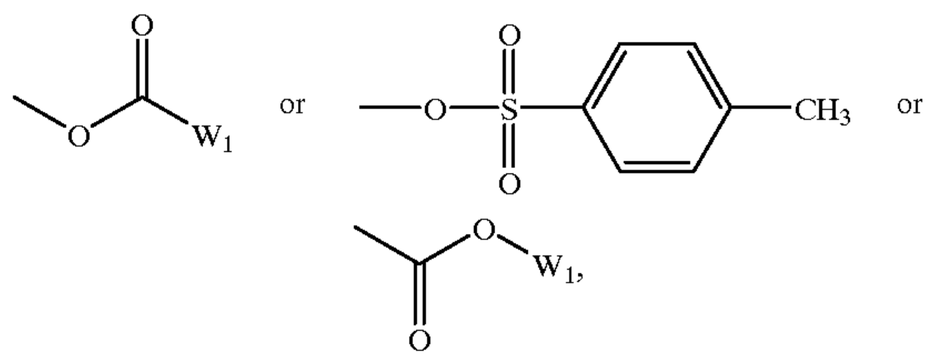
ether groups —$OSi(W_1)_3$, amino groups



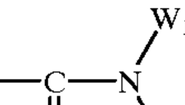
and amido groups



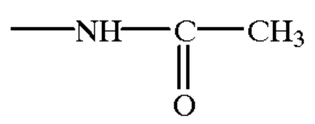
Z_2 represents a hydrogen atom, a benzyl group, a phenyl group optionally substituted by a substituent selected from a hydroxyl group, groups —CO—O—W_1, groups —O—CO—W_1, amino groups —$N(W_1)(W_2)$, amino groups —CO—N$(W_1)(W_2)$, amino groups —NH—CO—W_1 and a nitrile group; linear and branched C_1–C_8 alkyl groups optionally substituted by a substituent selected from a nitrile group, a carboxylic acid group, derivatives of a carboxylic acid group, a hydroxyl group, groups:



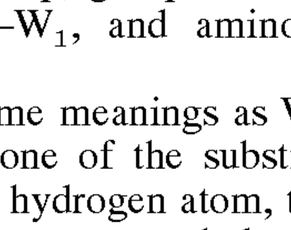
ether groups —$OSi(W_1)_3$, amino groups



and amido groups



or



Z_1 has the same meanings as Z_2 with the proviso that Z_1 is not methyl in the cases where T=H and X=CH,

W_1 and W_2, which are identical or different, are selected from a hydrogen atom and linear and branched C_1–C_4 alkyl groups,

W_4 is selected from a hydrogen atom and linear and branched C_1–C_4 alkyl groups, optionally substituted by at least one substituent selected from a hydroxyl group, groups —CO—O—W_1, groups —O—CO—W_1, and amino groups —$N(W_1)(W_2)$, and

W_3 has the same meanings as W_4 with the proviso that, when one of the substituents W_3 and W_4 represents a hydrogen atom, the other substituent does not represent a methyl or n-butyl group; and, when the substituents W_3 and W_4 are identical, they do not represent either a methyl group or an ethyl group.

8. A composition for the dyeing of keratin fibers comprising a cosmetically acceptable medium and an amount effective for dyeing keratin fibers of at least one dye chosen from:

6-(1-pentyl-1H-pyrrol-2-yl)quinoline-5,8-dione,

6-(1-benzyl-1H-pyrrol-2-yl)quinoline-5,8-dione,

methyl 4-(5,8-dioxo-5,8-dihydroquinolin-6-yl)-2,5-dimethyl-1H-pyrrole-3-carboxylate,

N-[2-[2-(5,8-dioxo-5,8-dihydroquinolin-6-yl)pyrrol-1-yl] ethyl]acetamide,

6-(1-phenyl-1H-pyrrol-2-yl)quinoline-5,8-dione,

3-[2-(5,8-dioxo-5,8-dihydroquinolin-6-yl)pyrrol-1-yl] propionitrile,

6-chloro-7-(1-methyl-1H-pyrrol-2-yl)quinoline-5,8-dione,

6-(1,2-dimethyl-1H-indol-3-yl)quinoline-5,8-dione,

6-(1-benzyl-1H-indol-3-yl)quinoline-5,8-dione,

6-[p-(N,N-(2-diacetyloxyethyl)amino)phenyl]-quinoline-5,8-dione,

6-(2-phenyl-1H-indol-3-yl)quinoline-5,8-dione,

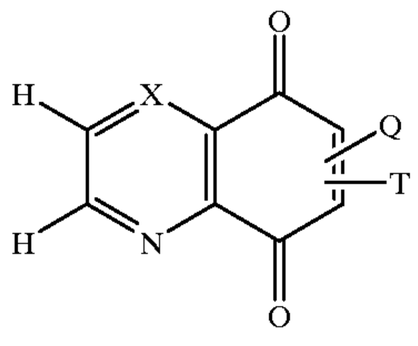
6-(1-methyl-1H-indol-3-yl)quinoline-5,8-dione,

6-(2-methyl-1H-indol-3-yl)quinoline-5,8-dione, and

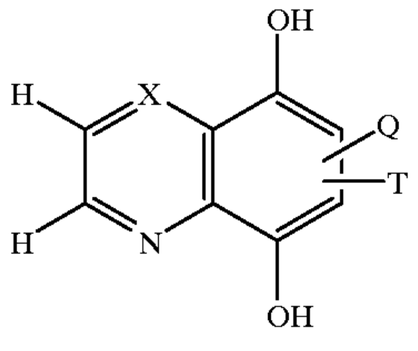
6-(1-methyl-1H-pyrrol-2-yl)quinoxaline-5,8-dione.

9. A composition for the dyeing of keratin fibers comprising a cosmetically acceptable medium and an amount effective for dyeing keratin fibers of at least one dye chosen from general formulae (III) and (IV) below:

(III)



(IV)

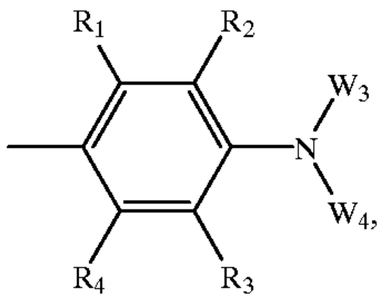


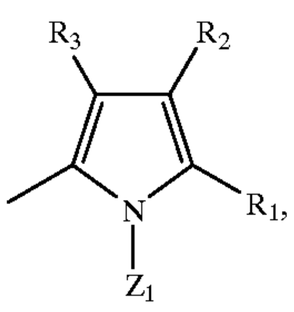
wherein,

X is chosen from —CH and —N;

T is a hydrogen atom;

Q is chosen from formulae below:





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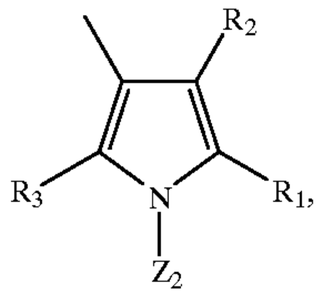
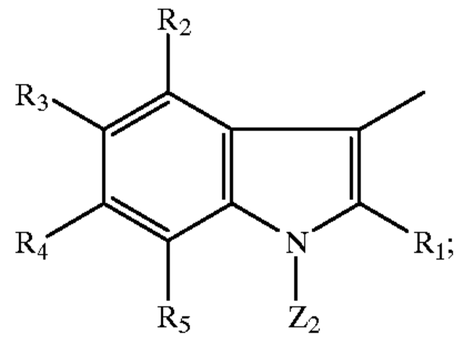


and



wherein further,

R_1 is chosen from —H and —CH_3 groups;

R_2 is chosen from —H and —COO—W_1 groups;

R_3 is chosen from —H and methyl groups;

R_4 and R_5 are both H;

W_1 is a —CH_3 group;

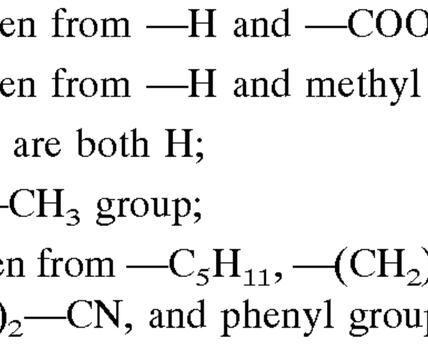
Z_1 is chosen from —C_5H_{11}, —$(CH_2)_2$—NH—$COCH_3$, —$(CH_2)_2$—CN, and phenyl groups;

Z_2 is chosen from —H, —CH_3, and benzyl groups; and

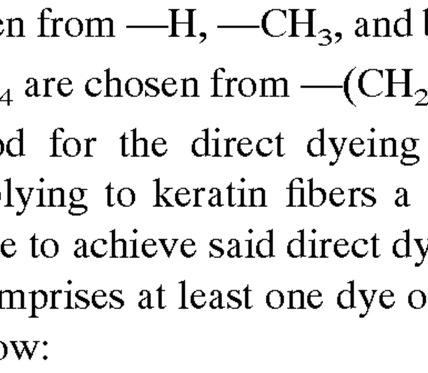
W_3 and W_4 are chosen from —$(CH_2)_2OCOW_1$ groups.

10. A method for the direct dyeing of keratin fibers, comprising applying to keratin fibers a composition in an amount effective to achieve said direct dyeing, wherein said composition comprises at least one dye of general formulae (I) and (II) below:

(I)



(II)

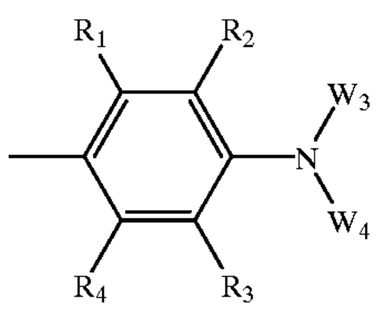


wherein:

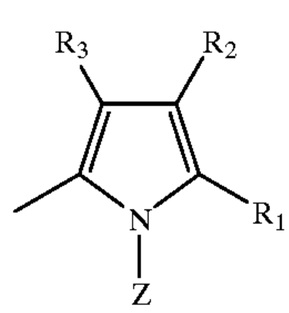
T is chosen from a hydrogen atom, halogen atoms and a hydroxyl group;

X is chosen from a —CH group and a nitrogen atom;

Q is chosen from the groups below:



or



or

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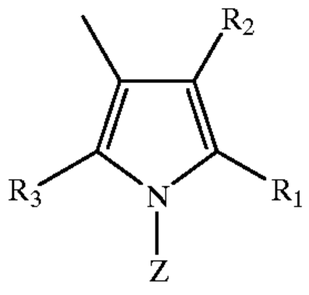
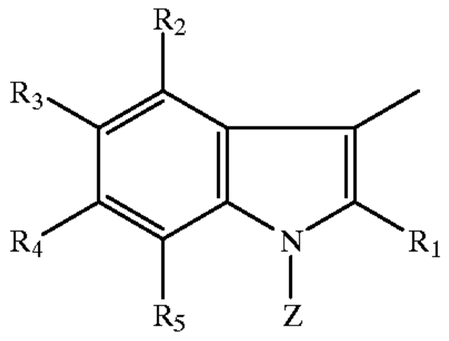
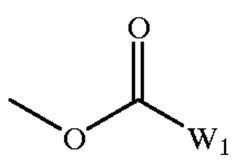
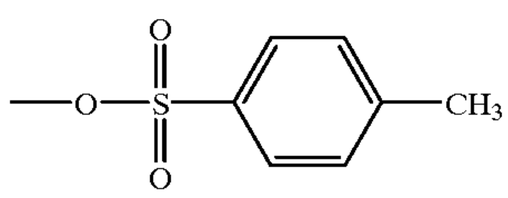
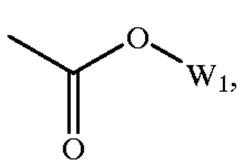
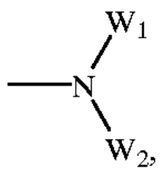



wherein in said groups:

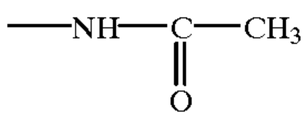
R_1, R_2, R_3, R_4 and R_5, which are identical or different, are selected from a hydrogen atom, C_1–C_4 alkoxy groups, amino groups —$N(W_1)(W_2)$, groups —NH—CO—W_1, groups —O—CO—W_1, a hydroxyl group, a carboxylic acid group, derivatives of a carboxylic acid group, halogen atoms, linear and branched C_1–C_4 alkyl groups optionally substituted by a substituent selected from nitrile groups, a carboxylic acid group, derivatives of a carboxylic acid group, a hydroxyl group, groups:

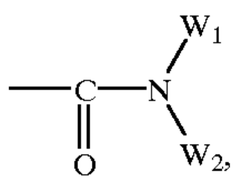
ether groups —$OSi(W_1)_3$, amino groups



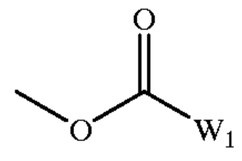
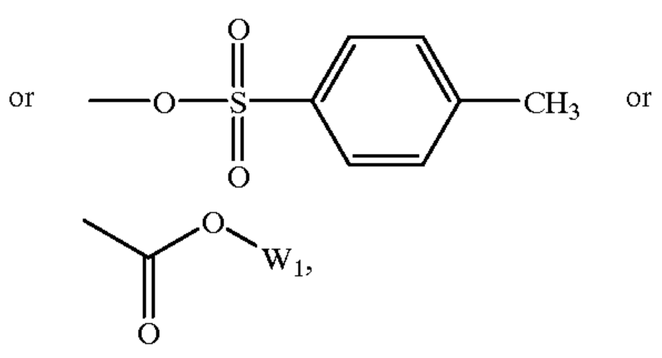
and amido groups



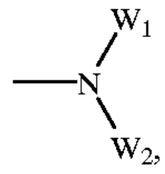
or



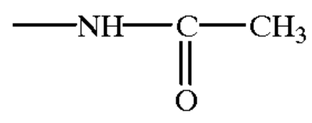
Z is selected from a hydrogen atom, a benzyl group, a phenyl group optionally substituted by a substituent selected from a hydroxyl group, groups —O—CO—W_1, amino groups —$N(W_1)(W_2)$, groups —NH—CO—W_1 and a nitrile group; linear and branched C_1–C_8 alkyl groups optionally substituted by a substituent selected from a nitrile group, a carboxylic acid group, derivatives of a carboxylic acid group, a hydroxyl group, groups:

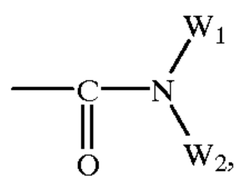
ether groups —$OSi(W_1)_3$, amino groups



and amido groups



or

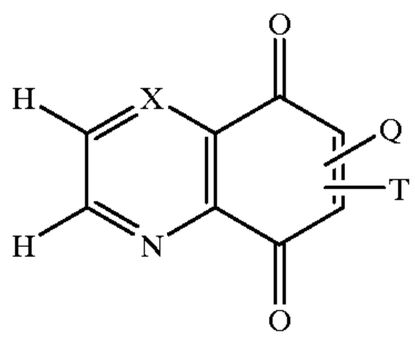


W_1 and W_2, which are identical or different, are selected from a hydrogen atom and linear and branched C_1–C_4 alkyl groups,

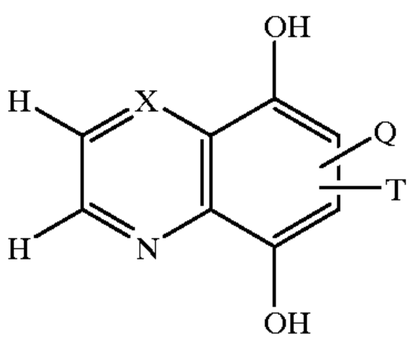
W_3 and W_4, which are identical or different, are selected from a hydrogen atom and linear and branched C_1–C_4 alkyl groups optionally substituted by at least one substituent selected from a hydroxyl group, groups —CO—O—W_1, groups —O—CO—W_1, and amino groups —$N(W_1)(W_2)$.

11. A composition for the oxidation dyeing of hair comprising a cosmetically acceptable medium and an amount effective for dyeing hair of at least one direct dye chosen from general formulae (I) and (II) below:

(I)



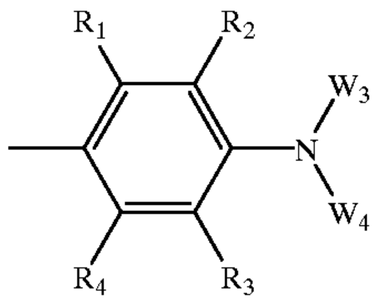
(II)



wherein:

T is chosen from a hydrogen atom, halogen atoms and a hydroxyl group;

X is chosen from a —CH group and a nitrogen atom;
Q is chosen from the groups below: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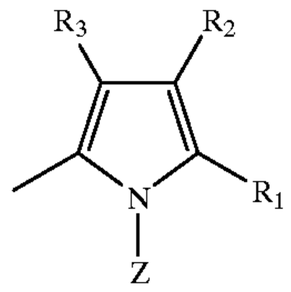
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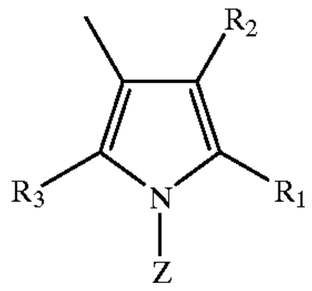
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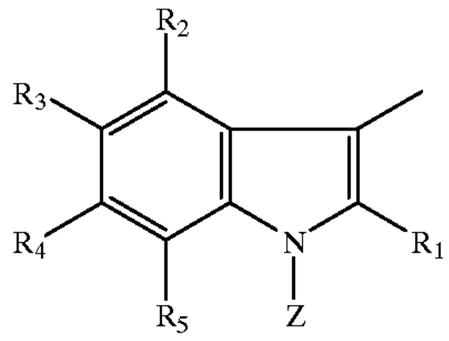
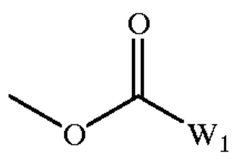


wherein in said groups:

R_1, R_2, R_3, R_4 and R_5, which are identical or different, are selected from a hydrogen atom, C_1–C_4 alkoxy groups, amino groups —$N(W_1)(W_2)$, groups —NH—CO—W_1, groups —O—CO—W_1, a hydroxyl group, a carboxylic acid group, derivatives of a carboxylic acid group, halogen atoms, linear and branched C_1–C_4 alkyl groups optionally substituted by a substituent selected from nitrile groups, a carboxylic acid group, derivatives of a carboxylic acid group, a hydroxyl group, groups: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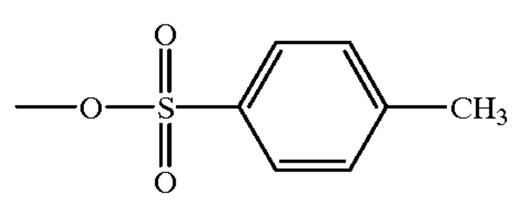
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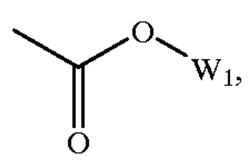
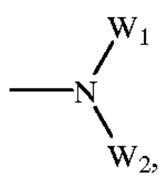
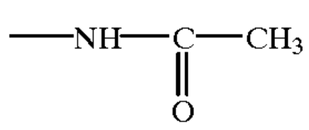


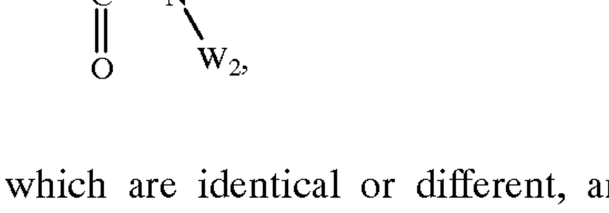
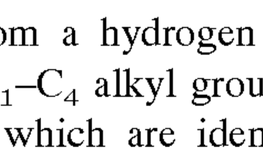
ether groups —$OSi(W_1)_3$, amino groups



and amido groups

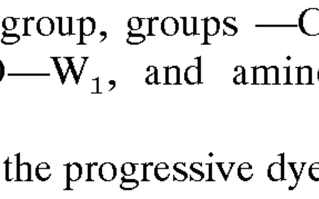


Z is selected from a hydrogen atom, a benzyl group, a phenyl group optionally substituted by a substituent selected from a hydroxyl group, groups —O—CO—W_1, amino groups —$N(W_1)(W_2)$, groups —NH—CO—W_1 and a nitrile group; linear and branched C_1–C_8 alkyl groups optionally substituted by a substituent selected from a nitrile group, a carboxylic acid group, derivatives of a carboxylic acid group, a hydroxyl group, groups:

or

or


ether groups —$OSi(W_1)_3$, amino groups

and amido groups



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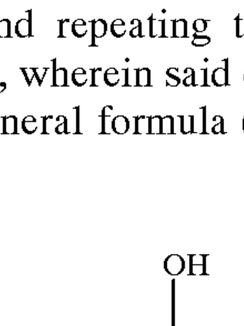
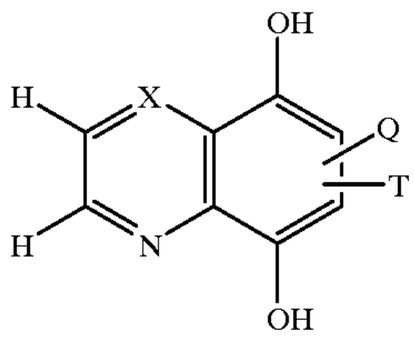


W_1 and W_2, which are identical or different, are selected from a hydrogen atom and linear and branched C_1–C_4 alkyl groups,

W_3 and W_4, which are identical or different, are selected from a hydrogen atom and linear and branched C_1–C_4 alkyl groups optionally substituted by at least one substituent selected from a hydroxyl group, groups —CO—O—W_1, groups —O—CO—W_1, and amino groups —$N(W_1)(W_2)$.

12. A method for the progressive dyeing of keratin fibers, comprising applying a composition to said keratin fibers, exposing the fibers to atmospheric oxygen, rinsing and drying said fibers, and repeating the steps until desired coloration is achieved, wherein said composition comprises at least one dye of general formula (II) below:

(II)

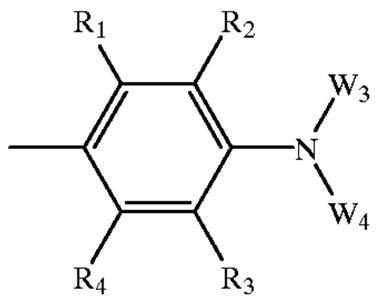


wherein:

T is chosen from a hydrogen atom, halogen atoms and a hydroxyl group;

X is chosen from a —CH group and a nitrogen atom;

Q is chosen from the groups below: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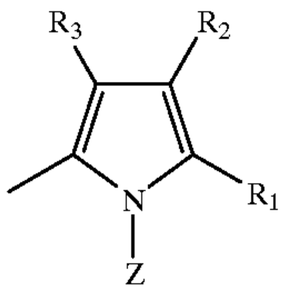
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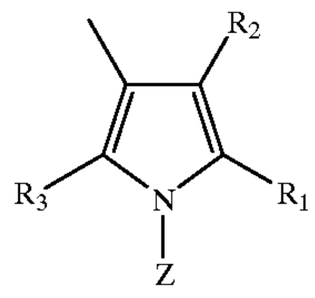
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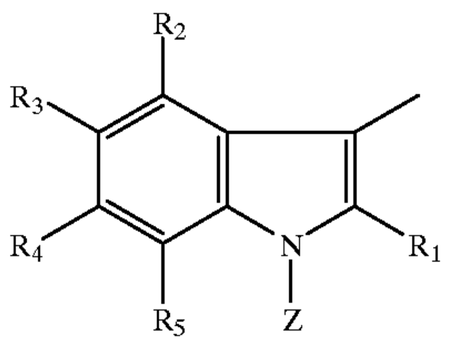
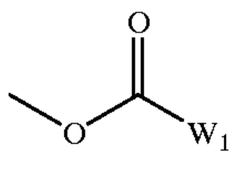


wherein in said groups:

R_1, R_2, R_3, R_4 and R_5, which are identical or different, are selected from a hydrogen atom, C_1–C_4 alkoxy groups, amino groups —$N(W_1)(W_2)$, groups —NH—CO—W_1, groups —O—CO—W_1, a hydroxyl group, a carboxylic acid group, derivatives of a carboxylic acid group, halogen atoms, linear and branched C_1–C_4 alkyl groups optionally substituted by a substituent selected from nitrile groups, a carboxylic acid group, derivatives of a carboxylic acid group, a hydroxyl group, groups: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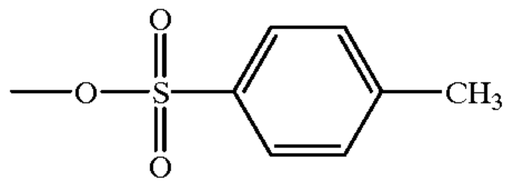
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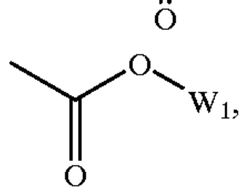
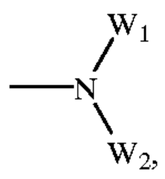
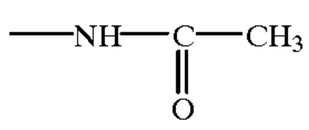


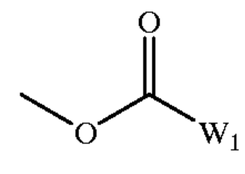
ether groups —$OSi(W_1)_3$, amino groups



and amino groups



Z is selected from a hydrogen atom, a benzyl group, a phenyl group optionally substituted by a substituent selected from a hydroxyl group, groups —O—CO—W_1, amino groups —$N(W_1)(W_2)$, groups —NH—CO—W_1 and a nitrile group; linear and branched C_1–C_8 alkyl groups optionally substituted by a substituent selected from a nitrile group, a carboxylic acid group, derivatives of a carboxylic acid group, a hydroxyl group, groups: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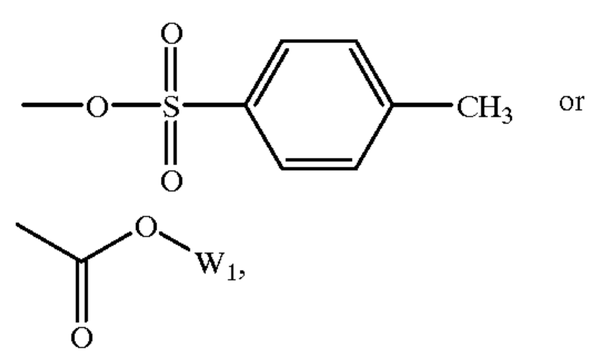
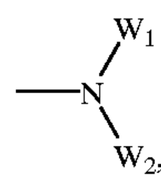
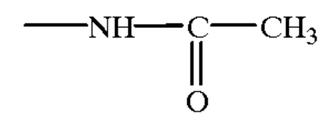

or

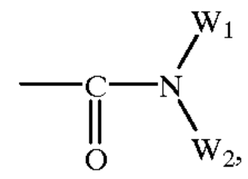
ether groups —$OSi(W_1)_3$, amino groups



and amido groups



or

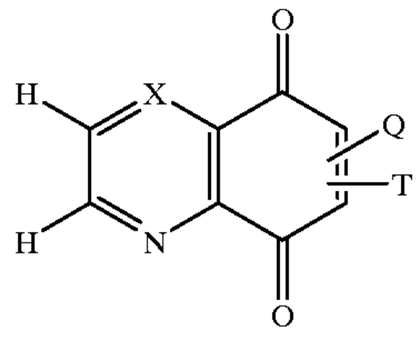


W_1 and W_2, which are identical or different, are selected from a hydrogen atom and linear and branched C_1–C_4 alkyl groups,

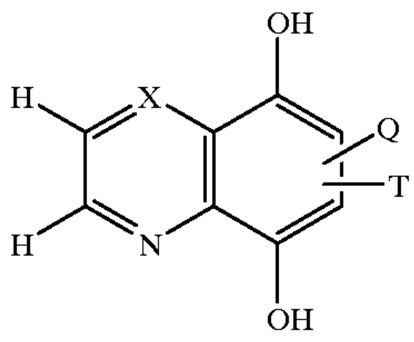
W_3 and W_4, which are identical or different, are selected from a hydrogen atom and linear and branched C_1–C_4 alkyl groups optionally substituted by at least one substituent selected from a hydroxyl group, groups —CO—O—W_1, groups —O—CO—W_1, and amino groups —$N(W_1)(W_2)$.

13. A compound selected from formulae (I) and (II) below:

(I)



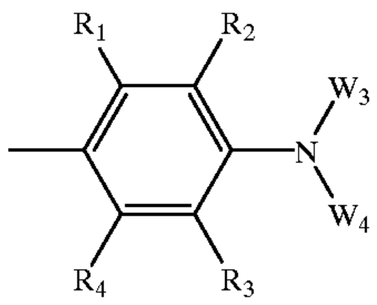
(II)



wherein:

T is chosen from a hydrogen atom, halogen atoms and a hydroxyl group;

X is chosen from a —CH group and a nitrogen atom;
Q is chosen from the groups below: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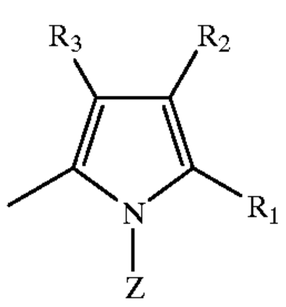
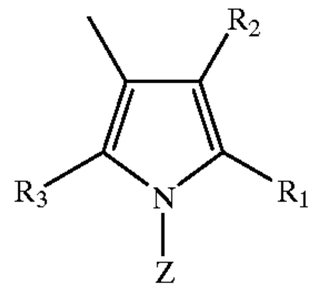
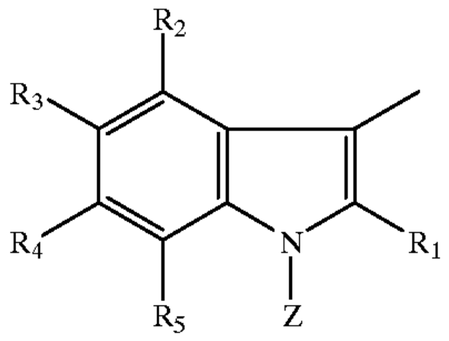
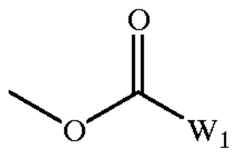

or

or


wherein in said groups:
R_1, R_2, R_3, R_4 and R_5, which are identical or different, are selected from a hydrogen atom, C_1–C_4 alkoxy groups, amino groups —$N(W_1)(W_2)$, groups —NH—CO—W_1, groups —O—CO—W_1, a hydroxyl group, a carboxylic acid group, derivatives of a carboxylic acid group, halogen atoms, linear and branched C_1–C_4 alkyl groups optionally substituted by a substituent selected from nitrile groups, a carboxylic acid group, derivatives of a carboxylic acid group, a hydroxyl group, groups: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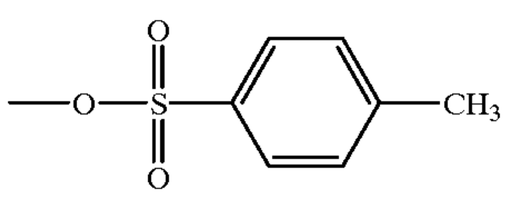
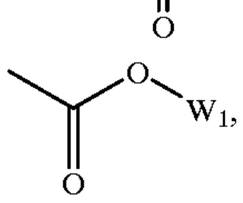
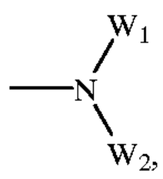
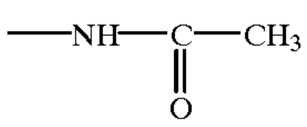

or


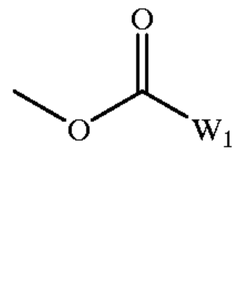
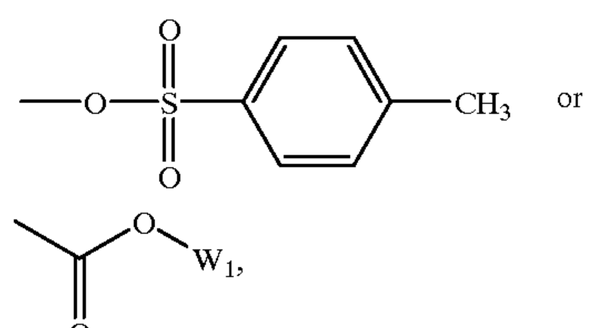
ether groups —$OSi(W_1)_3$, amino groups



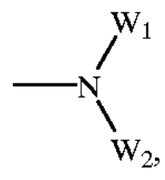
and amido groups



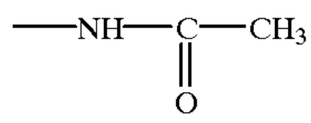
Z is selected from a hydrogen atom, a benzyl group, a phenyl group optionally substituted by a substituent selected from a hydroxyl group, groups —O—CO—W_1, amino groups —$N(W_1)(W_2)$, groups —NH—CO—W_1 and a nitrile group; linear and branched C_1–C_8 alkyl groups optionally substituted by a substituent selected from a nitrile group, a carboxylic acid group, derivatives of a carboxylic acid group, a hydroxyl group, groups:


or

or

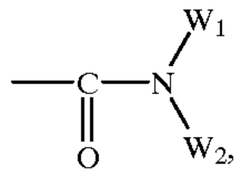

ether groups —$OSi(W_1)_3$, amino groups



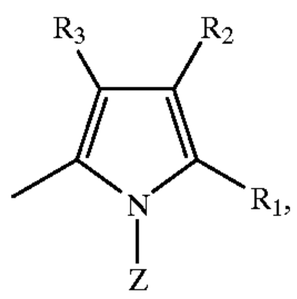
and amido groups



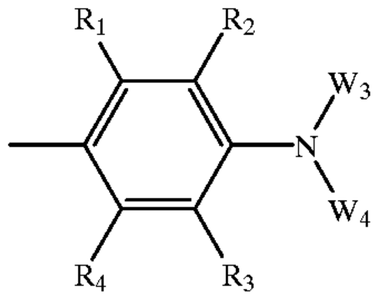
or



W_1 and W_2, which are identical or different, are selected from a hydrogen atom and linear and branched C_1–C_4 alkyl groups,
W_3 and W_4, which are identical or different, are selected from a hydrogen atom and linear and branched C_1–C_4 alkyl groups optionally substituted by at least one substituent selected from a hydroxyl group, groups —CO—O—W_1, groups —O—CO—W_1, and amino groups —$N(W_1)(W_2)$ with the proviso that:
when Q represents

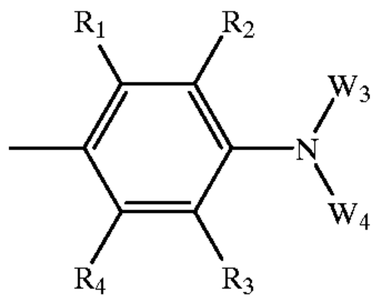


X=CH and T=H, then Z is other than the methyl group;
when Q represents



and one of the substituents W_3 and W_4 represents a hydrogen atom, the other substituent does not represent a methyl or n-butyl group; and

when Q represents



and the substituents W_3 and W_4 are identical, they do not represent either a methyl group or an ethyl group.

14. A compound selected from the following compounds:

6-(1-pentyl-1H-pyrrol-2-yl)quinoline-5,8-dione,

6-(1-benzyl-1H-pyrrol-2-yl)quinoline-5,8-dione,

methyl 4-(5,8-dioxo-5,8-dihydroquinolin-6-yl)-2,5-dimethyl-1H-pyrrole-3-carboxylate,

N-[2-[2-(5,8-dioxo-5,8-dihydroquinolin-6-yl)pyrrol-1-yl] ethyl]acetamide,

6-(1-phenyl-1H-pyrrol-2-yl)quinoline-5,8-dione,

3-[2-(5,8-dioxo-5,8-dihydroquinolin-6-yl)pyrrol-1-yl] propionitrile,

6-chloro-7-(1-methyl-1H-pyrrol-2-yl)quinoline-5,8-dione,

6-(1,2-dimethyl-1H-indol-3-yl)quinoline-5,8-dione,

6-(1-benzyl-1H-indol-3-yl)quinoline-5,8-dione,

6-[p-(N,N-(2-diacetyloxyethyl)amino)phenyl]-quinoline-5,8-dione,

6-(2-phenyl-1H-indol-3-yl)quinoline-5,8-dione,

6-(1-methyl-1H-indol-3-yl)quinoline-5,8-dione,

6-(2-methyl-1H-indol-3-yl)quinoline-5,8-dione,

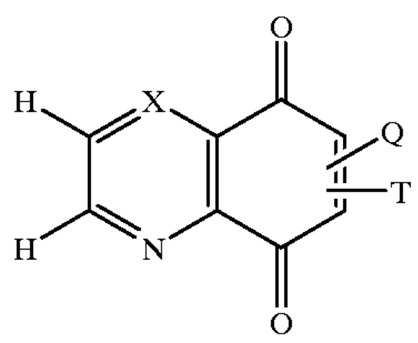
6-(1-methyl-1H-pyrrol-2-yl)quinoxaline-5,8-dione.

15. A method of dyeing human keratinous fibres comprising applying a dyeing composition of claim **1** to the keratinous fibres and, after a time sufficient to develop a desired colouration, rinsing the fibres, washing the fibres, rinsing again and drying.

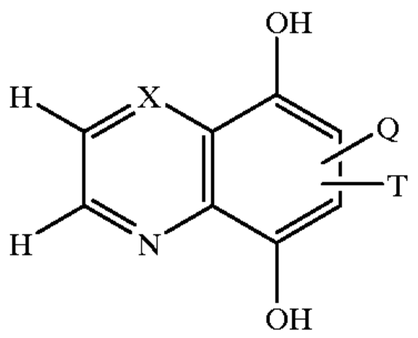
16. A method of dyeing human keratinous fibres comprising applying a dyeing composition of claim **1** to the keratinous fibres for a time sufficient to develop a desired colouration without final rinsing.

17. A compound selected from formulae (I) and (II) below:

(I)



(II)

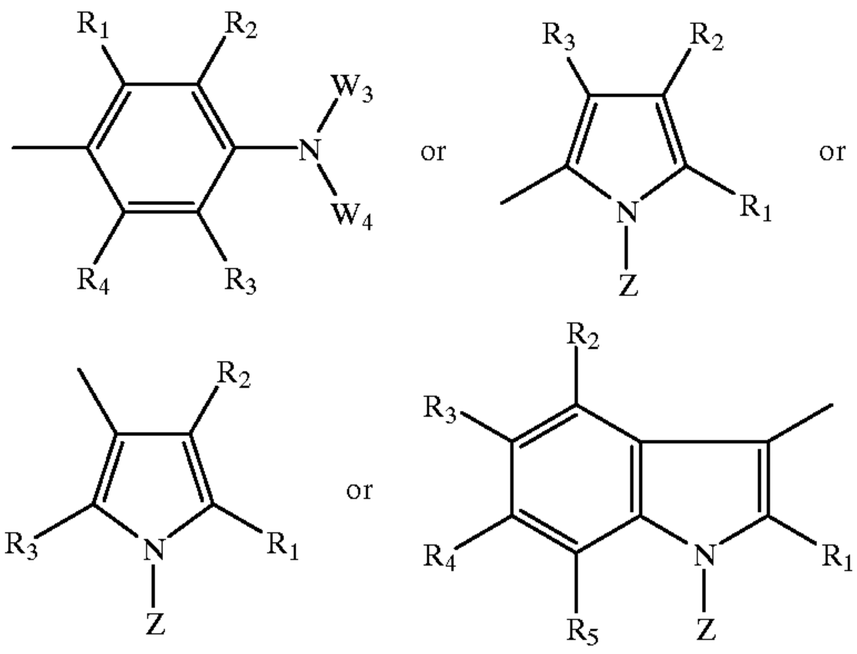


wherein:

T is chosen from a hydrogen atom, halogen atoms and a hydroxyl group;

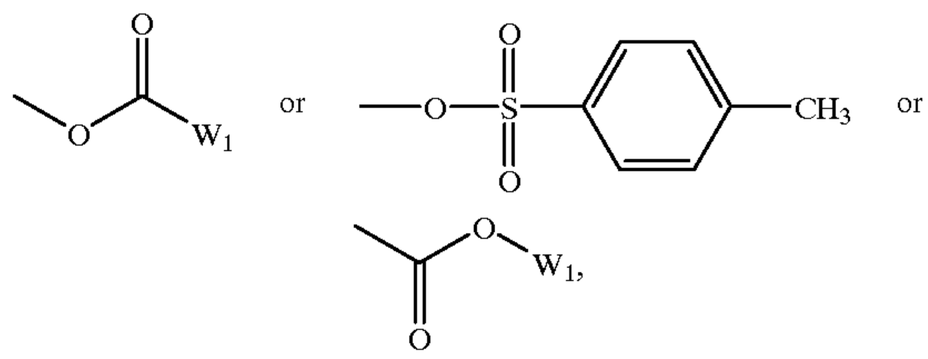
X is chosen from a —CH group and a nitrogen atom;

Q is chosen from the groups below:

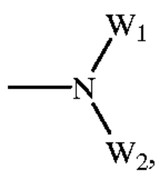


wherein in said groups:

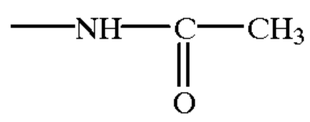
R_1, R_2, R_3, R_4 and R_5, which are identical or different, are selected from a hydrogen atom, C_1–C_4 alkoxy groups, amino groups —$N(W_1)(W_2)$, groups —NH—CO—W_1, groups —O—CO—W_1, a hydroxyl group, a carboxylic acid group, derivatives of a carboxylic acid group, halogen atoms, linear and branched C_1–C_4 alkyl groups optionally substituted by a substituent selected from nitrile groups, a carboxylic acid group, derivatives of a carboxylic acid group, a hydroxyl group, groups:



ether groups —$OSi(W_1)_3$, amino groups

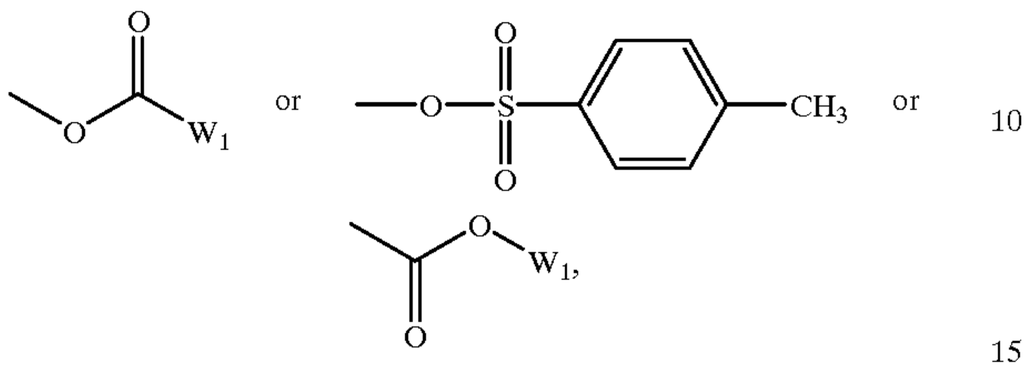


and amido groups

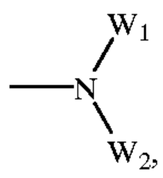


Z is selected from a hydrogen atom, a benzyl group, a phenyl group optionally substituted by a substituent selected from a hydroxyl group, groups

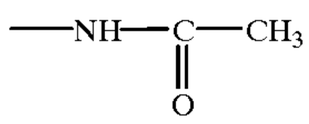
—O—CO—W_1, amino groups —N(W_1)(W_2), groups —NH—CO—W_1 and a nitrile group; linear and branched C_1–C_8 alkyl groups optionally substituted by a substituent selected from a nitrile group, a carboxylic acid group, derivatives of a carboxylic acid group, a hydroxyl group, groups:



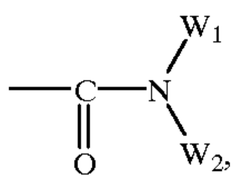
ether groups —$OSi(W_1)_3$, amino groups



and amido groups



or

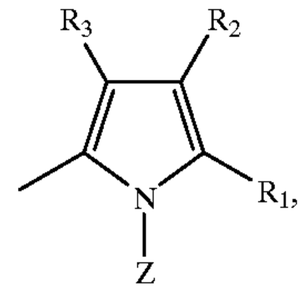


W_1 and W_2, which are identical or different, are selected from a hydrogen atom and linear and branched C_1–C_4 alkyl groups,

W_3 and W_4, which are identical or different, are selected from a hydrogen atom and linear and branched C_1–C_4 alkyl groups optionally substituted by at least one substituent selected from a hydroxyl group, groups —CO—O—W_1, groups —O—CO—W_1, and amino groups —N(W_1)(W_2)

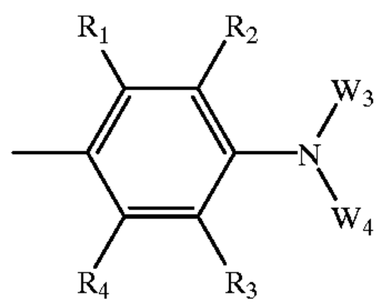
with the proviso that:

when Q represents



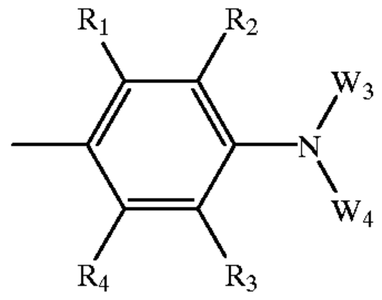
X=CH and T=H, then Z is other than the methyl group;

Q does not represent



in formula (I); and

when Q represents



in formula (II) and the substituents W_3 and W_4 are identical, they do not represent a methyl group.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 6,391,064 B1
DATED : May 21, 2002
INVENTOR(S) : Richard Baudry et al.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Title page,
Item [54], in the title "**QUINOLINE-5, 8-DIONES**" should read -- **QUINOLINE-5,8-DIONES** --;

Column 18,
Line 20, after the third structure from the top of the column, insert -- or --;

Column 19,
Line 42, "quinotine" should read -- quinoline --;

Column 27,
Line 54, after the second structure from the bottom of the column, insert -- or --;

Column 29,
Line 48, "amino" should read -- amido --;
Line 54, after the second structure from the bottom of the column, insert -- or --;

Column 31,
Line 54, after the second structure from the bottom of the column, insert -- or --; and

Column 34,
Line 58, after the second structure from the bottom of the column, insert -- or --.

Signed and Sealed this

Seventeenth Day of September, 2002

Attest:

JAMES E. ROGAN
Director of the United States Patent and Trademark Office

Attesting Officer